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CONTINUOUS LIQUEFACTION OF HAT CREEK COAL

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1.0 SUMMARY

This report presents results from a program of continuous liquefaction tests on Hat Creek coal, with continuous hydrotreating of primary liquids followed by distillation and recycle of +200°C liquid as process solvent.

The program was funded on a 50/50 basis by the B.C. Government (Ministries of Energy, Mines and Petroleum Resources and Universities Science and Communications) and CANMET.

Technical objectives of the study were: confirmation of high ($\geq$90%) batch test coal conversions in a continuous system; investigation of primary liquid product quality; evaluation of continuous, fixed bed catalytic hydrotreating of primary liquid product and evaluation of a heterogeneous catalyst for primary liquefaction.

The initial series of continuous liquefaction tests (without added catalyst) did not result in either stable recycle operation or satisfactory conversions. Following these test sequences, modifications were made to the reactor agitator, feed inlet and hydrogen flow rate.

After these modifications, sequences of continuous tests with product hydrotreatment and solvent recycle were done on coal samples with iron (catalyst) added by ion exchange of coal with ferrous sulphate solutions. These test sequences resulted in satisfactory conversion ($\geq$90% by ash balance, 90 - 96% by calorific value), thereby confirming that the continuous system can give conversions equivalent to batch tests. The program budget did not allow repeating of non-catalyzed tests in the modified system, so the results do not allow comparison of catalytic vs noncatalytic liquefaction.

During the program, the continuous fixed bed hydrotreater was modified to operate in an upflow mode which was found to be superior to downflow operation with respect to temperature control, operability and catalyst stability.

Comparison of results from upflow hydrotreater tests with fresh catalyst and at a catalyst age of 60 (feed:catalyst, w/w) indicates no significant deactivation. Naphtha (ibp - 200°C) contents of hydrotreated primary liquids were high (12-24 wt %), and very high (40 - >75%) in relation to dry ash free (daf) coal.

Byproduct gas yields from high conversion tubing bomb (batch) tests indicate that C_1-C_4 hydrocarbon gases account for up to 16.4% of product on a calorific value basis.

Overall, these results indicate the net product slate from the approach tested would consist of naphtha and LPG(C_2-C_4 hydrocarbons). Alternately, reforming of LPG as well as by-product methane could make the operation independent of external hydrogen sources.

Coal beneficiation (ash rejection) obtained by the iron catalyst impregnation procedure is compared to results obtained elsewhere by conventional coal washing.

A preliminary economic analysis based on test data for the lowest grade coal sample indicates a favourable (3.06-3.85) ratio of product value to raw material cost.

2.0 INTRODUCTION

2.1 Background

Under a provincially funded program initiated in 1979, B.C. Research developed test facilities for direct coal liquefaction and performed an experimental survey of provincial coal resources to determine relative potential for direct liquefaction of coal types and specific deposits available within the province. Results of this work [1] identified Hat Creek sub-bituminous coal as a good potential feedstock for direct liquefaction due to a combination of factors including:

- high conversions, up to 95% (w/w, daf basis) under batch test conditions.

- very large single site reserves ($\simeq 5 \times 10^9$ tonnes proven and drill indicated)

- good location with respect to transport (pipelines, rail, highway), social infrastructure and ports.

A necessary followup to the batch testwork was considered to be confirmation of yield and product quality in a continuous system which was built and used for preliminary tests under the provincially funded program.

In November, 1982, a proposal was issued in response to a general solicitation by CANMET for projects under the Shared Cost Energy Research program. A specific Request for Proposal was subsequently received for the proposed work and a contract awarded in June, 1983.

This report presents results of work conducted.

2.2 Objectives

As specified in the Request for Proposal[2], technical objectives of the program were:

- to confirm high liquid yields (indicated by tubing bomb test data) in a continuous liquefaction system operated at ~600 g coal/h (2000 g feed slurry/h; nominal residence time ~0.5 h).

- to determine liquid quality and yield under a range of continuous test conditions

- to investigate effects of catalytic solvent pre-hydrogenation on liquid yield/product quality (with/without bottoms recycle)

- to investigate fixed bed catalytic hydrogenation of heavy (asphaltene and preasphaltene) products for production of recycle solvent and/or final product

- to investigate effects of appropriate heterogeneous catalysts on conversion in the continuous system

- to provide a comprehensive report of all test results, conclusions and recomendations regarding technical aspects of direct liquefaction of Hat Creek coal.

3.0 MATERIALS AND METHODS

3.1 Test Coals

Coal samples for testing were obtained by channel sampling of bulk coal stockpiles at the minesite. These stockpiles were established by B.C. Hydro and Power Authority Ltd. (leaseholder for the deposit) as part of a major sampling effort. The stockpiles, designated "Trench A" and "Trench B" were taken from large exploration pits; they represent major zones of the proven, mineable reserves of the deposit.

Samples were bagged and labelled at the site. In the laboratory, Trench A and Trench B samples were separately bulk blended, air dried, crushed through jaw and gyratory crushers, riffle split and rebagged in a ~10 kg subsamples for storage.

As required for testwork, subsamples were recovered from storage, impact milled in a CO_2 atmosphere to 150 microns (<100 mesh) and subsampled for analysis.

For non-catalyzed liquefaction tests, 150 micron material was slurried with solvent and passed through a vibratory ball mill for final comminution.

For tests involving iron catalyst added by ion exchange[3] the following procedure was evolved:

- slurry 40 kg coal (-150 micron) with 200 l tapwater and 15 kg technical $FeSO_4.4H_2O$
- agitate for 48 h and settle overnight
- decant solution and non-settling fines to separate vessel

- repulp with 3 x 100 l tapwater, settle and decant
- transfer settled ("coarse") solids to tray and dry at 40°C (in air)
- pass dried material through impact mill under CO_2 to break up agglomerates
- slurry with solvent and proceed to vibration milling.

3.2 Liquefaction Solvent

Commercial creosote and anthracene oils purchased from Crawley Tar Ltd. were the starting materials for all tests. These raw materials were prepared by hydrotreating and distillation as described in the following sections.

3.3 Reagents

Reagents used in sample processing were tetrahydrofuran, carbon disulphide and toluene; technical grades were used except as specifically noted.

Reagent grade chemicals were used in preparation of standard mixtures for calibration of the capillary gas chromatograph used in analysis of liquid samples.

3.4 Tubing Bomb System

The "tubing bomb" microautoclave batch test facility is shown schematically in Figure 1. The system and method of operation have been described previously[4].

3.5 Continuous Liquefaction System

The bench scale liquefaction system is shown schematically as Figure 2. The feed system is of conventional design. It consists of agitated slurry feed tank (load cell mounted), a Moyno pump to provide feed circulation and a two-head Bran & Lubbe high pressure piston pump which delivers slurry to the reactor. The reactor is a 2 l Autoclave Engineers Autoclave with magnedrive agitator. During the initial part of the contract period, the agitator was a 5 cm diameter, 45° pitch, 3 blade propellor; this was subsequently replaced with a 2.5 cm diameter, four blade turbine.

The product receiver system consists of two parallel trains, each conprising 2 l and 250 ml autoclaves in series. Each train can be isolated, allowing it to be pressurized, depressurized and drained independently. In operation, reactor product is directed alternately to each of these trains. While one train is on line and accumulating slurry product, the other is partially depressurized, drained of slurry and repressurized. This feature eliminates the necessity for throttling of slurry or slurry - gas flows from reactor pressure to atmospheric pressure.

During the contract period, reactor pressure was maintained with a cylinder regulator; hydrogen exhaust gas flow was controlled manually with a needle valve and rotameter.

Operational producedures are described in Appendix 1 and the bulk product workup procedure is presented in Appendix 2.

3.6 Continuous Hydrotreater

The fixed bed continuous hydrotreater used in the study is shown schematically as Figure 3. The load cell mounted feed tank is

located above the high pressure Bran & Lubbe feed pump to provide primary pressure. Pressurized liquid feed passes through a preheater and joins the hydrogen feed at the base of the reactor column. Note that the hydrotreater was operated in an upflow mode throughout the contract period. The reactor (5 cm diameter x 2m, 316 stainless steel tube) is heated by three independently controlled electrical clamshell heaters. Reactor outflow (liquid, vapour and gas) passes to a 20 l receiver vessel (gas cylinder) for cooling and phase separation. Outflow gas, controlled manually by needle valve, passes to an exterior vent.

Hydrogen flow was monitored by a mass flow meter and reactor pressure controlled by a cylinder regulator.

Operational procedures are presented in Appendix 3; the manufacturer's catalyst presulphiding procedure is presented in Appendix 4.

3.7 Analytical Procedures

3.7.1 Slurry Feed and Products

For tubing bomb tests, product slurry was washed out with tetrahydrofuran and filtered on tared glass fibre (0.45μ) pads. Filter cakes were washed with THF at ambient temperature, vacuum dried and weighed to determine solid residue. THF soluble product was diluted to a fixed volume (normally 100 ml) with THF; aliquot samples of this solution were further diluted with carbon disulphide before capillary gas chromatography using a Hewlett Packard instrument with a 15 m capillary column and flame ionization detector.

For thermogravimetric analyses (TGA) using a Dupont 1080 unit, aliquot sampes of THF solubles were evaporated under vacuum at

~40°C; samples of remaining liquid were transferred to the TGA balance pan using a syringe. TGA analyses of THF extract and hydrotreater liquid product were done under flowing nitrogen with programmed temperature increase of 20°C/minute to 325°C for estimation of true distillables or to 525°C for estimation of carbon or coke residue. Proximate analyses of THF insolubles were done by TGA after manual removal of the filter cake from the pad and mixing. Calorific values were determined for separate subsamples of residue using a Parr calorimeter.

Slurry product from the continuous reactor was analyzed in a similar manner, except that weighed aliquot samples were used.

Reactor feed slurry was analyzed by THF filtration of weighed samples to confirm feed solids content.

3.7.2 Gas Analysis

For most of the contract period, gas samples from all reactors were taken in pressure cylinders for auto-injection and chromatographic analysis using the Hewlett Packard instrument. At the end of the study, this procedure was modified for tubing bomb tests to venting the bomb and its gas line into a sample bag at atmospheric pressure. From the bag, a subsample was transferred to the chromatograph injection loop by connecting the sample bag port to an injection tube followed by flushing and filling the injection loop using manual pressure on the bag.

Gases measured directly by GC were N_2, O_2, CO, CO_2 and C_1-C_4 hydrocarbons; hydrogen was normally measured by difference.

3.8 Conversion Calculations

Conversion data are presented for both gravimetric and calorific conversion of coal. For samples from the continuous system, both

methods rely on (TGA determined) ash content of insoluble residue. For tubing bomb tests, the total residue weight is used.

Sample calculations are presented as Appendix 5.

4.0 RESULTS AND DISCUSSION

4.1 Coal Sample Analyses

Results of proximate analyses on Trench "A" and "B" Hat Creek Coal samples used in current testwork are presented in Tables 1 and 2 respectively. These tables also include representative analyses of coarse (settled) and fine (decanted) material generated in ion exchange tests (see Section 3.1).

For both samples, the data show high moisture and ash contents characteristic of the Hat Creek deposit. Within this general range, the Trench A Material is significantly higher in ash (43.4 - 48%, dry basis) than the Trench B samples (27.9 - 35.2%), while as tested (essentially air dry) moisture contents are in the 18 - 22 wt% range for both coals.

For both Trench A and B samples, the iron ion exchange procedure resulted in (effective) beneficiation due to decantation of fine material. With reference to Table 1, dry basis ash content of Trench A coal was reduced from 43.4 to 31.3% while the fine reject contained 61.8% ash. Similarly, Trench B ash content was reduced from 35.2% to 26.2% (dry basis) with the fine reject containing 53% ash. A similar washing/decantation procedure without the ferrous sulphate (see Table 2, data for C-03-2 coarse and fine samples) showed a similar trend - i.e., ash concentrated in the fines - but the effect was not as strong as with ferrous sulphate present. This suggests that the ferrous sulphate additive has some effect on surface chemistry and sedimentation behaviour of the fine mineral matter present in the coal, as well as its physical/chemical sorption onto the coal organic matter.

These results are potentially of interest in relation to the possibility of cleaning Hat Creek Coals by agglomeration methods

[5, 6]. Pilot scale conventional (gravity) cleaning methods have been shown to be capable of producing clean coal of ~20% ash from blended Hat Creek raw coal [7]. If subsequent grinding and chemical treatment of the 20% ash gravity product could accomplish further cleaning, it would be desirable for conversion. Even the 20% of ash in gravity cleaned material would represent a heavy load with respect to reactor volume and particularly on liquid/solid separation.

4.2 Tubing Bomb Tests

Previously reported work (1) identified the following conditions for high conversion of Hat Creek coal in tubing bombs:

temperature 440°C
reaction time 25 min.
solvent: hydrotreated creosote (+200°C fraction)
solvent/coal ratio of 3:1
initial P_{H_2} :5.5 MPa
workup solvent:THF

Using these conditions, a series of locked cycle tests was performed in which liquefaction product (THF soluble material) was hydrotreated in batch (tubing bomb) tests with sulphided NiMo catalyst, then used as recycle solvent in the subsequent stage liquefaction test.

Results of locked cycle liquefaction tests on Trench B coal are presented in Table 3 and results of the corresponding product hydrotreating tests are presented in Table 4. In the liquefaction sequence, the first test (Bomb No. 465/4, Table 3) was done with +200°C non-hydrogenated creosote oil.

For the liquefaction test sequence, results of Table 3 show a large increase (from 55.4 to 88.6 wt %) in conversion from the first stage with non hydrogenated solvent to the second stage with hydrogenated solvent. The next two stages show no measurable trend in total conversion (89.4% and 90.0%) compared to the intial run with hydrotreated solvent. Similarly, there is no discernible trend in +525°C residue, gas production or hydrogen consumption after the second stage of recycle.

These data indicate that an effective recycle solvent can be prepared from the (THF soluble) liquid phase product.

Results of the associated batch hydrotreating tests are presented in Table 4. Hydrogen consumption could not be measured in these tests, since system pressure was maintained at 14 MPa by continuous make-up. It should be noted that the test conditions were as required (from previous test data) for ~50% conversion of naphthalene in raw creosote to tetralin. Increasing naphthalene to tetralin conversion through the test sequence (see Table 4, T:N ratios in product) reflects several factors including less hydrogen demand for sulphur removal and a decrease in 2 ring (naphthalene and derivatives) components relative to 3 and 4 ring aromatics.

The +525°C residue data (Table 4) for this test sequence clearly indicate that coke or carbon residue can be almost completely eliminated by a level of hydrotreatment which converts the raw liquid product into an acceptable donor solvent as shown by conversion results presented in Table 3.

The catalyst recovery data (Table 4) suggest very little coke formation, but carbon determinations were not done. Since the feed material for hydrogenation changed (i.e., approached solvent-coal equilibrium) through the test sequence, catalyst

activity cannot be defined from the data. However, the increasing T:N ratios in products suggests that the catalyst retained a major portion of its initial reactivity.

4.2.1 Gas Byproducts from Tubing Bomb Tests

Through most of the test program, byproduct gas yields were obtained by analyses of samples taken from the reactor under intermediate or full reactor pressure (2-14MPa). In all these tests, propane and butane were below detectable levels. Since these gases are of interest with respect to product slate, tubing bomb tests on feed slurry for continuous runs C-28 and C-29 (Trench B and A respectively, with iron catalyst)were conducted. Gas products from these test were vented to bags at atmospheric pressure and sampled by connecting the sample bag port to an injection tube followed by flushing and filling the injection loop of the chromatograph using manual pressure on the bag.

Results, presented in Table 5, were significantly different from previous tests in regard to total amounts of gas and relative proportion of methane and ethane. Propane was detected at a significant level, but butane was a very minor constituent.

The results presented in Table 5 show some inconsistency in nominally duplicate runs, particularly for methane/ethane and CO_2 yields in tests 535/1 and 2. In attempting to repeat these tests it was found that extremely careful handling is required to obtain reliable atmospheric pressure samples.

Table 6 presents byproduct gas yields for repeated experiments at 25 and 60 minute reaction times. From these data, it is clear that total conversion does not increase with reaction time beyond 25 minutes and that CO/CO_2 yields change only marginally with increasing reaction time.

For hydrocarbon gases, however, yields clearly increase with reaction time. For methane and ethane, increases in yield appear to be roughly proportional to reaction time. For C_3 and C_4 gases, yields are low or negligible at 25 minutes, but definitely significant at 60 minutes. Hydrogen consumption data (determined by difference, hence the least accurate) suggest a decreasing rate of hydrogen utilization with increasing reaction time.

4.3 Continuous Liquefaction Tests

4.3.1 Continuous Liquefaction Tests without Catalyst

4.3.1.1 Trench B Coal

Results of continuous liquefaction tests on Trench B coal without added catalyst are presented in Table 7. In considering these results, it should be noted that this was the first attempt to duplicate the batch test data on solvent hydrogenation/recycle in the continuous system, and the work was done immediately after the hydrotreater was modified from downflow to upflow operation. Thus consistent solvent hydrogenation was not obtained. These results represent the start of what can be described as a learning curve.

In this test sequence (Table 7), startup solvent was prepared initially by hydrotreating a 2:1 mixture of creosote oil and anthracene oil. This mixture was chosen in order to start with a higher boiling or "heavier" mixture which was expected to be a closer approximation of primary coal liquid than the (lighter) creosote alone. This approach was abandoned after Run C-11 in favour of distilling the hydrotreated solvent to remove naphtha (material boiling below 200°C).

The runs (Table 7) fall into two general groups as follows:

First Recycle Sequence:	startup;	C-7, C-8
	recycle #1;	C-10
	recycle #2;	C-13
Second Recycle Sequence:	startup;	C-11, C-12
	recycle #1a;	C-16
	recycle #2a;	C-17
	recycle #3a;	C-18

The two sequences were carried as far as C-13 to provide backup recycle material in case of the loss due to operational problems which were occuring consistently during this phase of the study. After C-13, the hydrotreater was undergoing maintenance and an unsuccessful attempt was made to hydrogenate the C-13 product using a (pulverized) catalyst/product slurry feed to the continuous autoclave unit. At this point, the first sequence was abandoned.

The second sequence was carried through four stages, with generally unfavourable results except for the first recycle (C-16) in which a conversion of 86.7% was obtained. In the second recycle (C-17), conversion dropped to 74.3% and in the third cycle (C-18) conversion was only 63.1%.

At the time the work was done, this steady decline in conversion was attributed to inconsistent hydrotreater operation which was certainly a major factor. For example, with reference to Table 7, T:N ratios varied from 0.76 to 2.65 in the second recycle sequence. The batch recycle test data (Table 3) showed good conversion at T:N ratios up to 3, but solvent hydrogenation through the batch sequence was much better controlled and fully isothermal. Retention time and short circuiting were also con-

sidered to be important, especially since C-16 (86.7% conversion) was done at a low feedrate. During this phase of the study, operating control of feedrate was not good; the average feedrates (Table 7) include periods of no flow (generally due to pump blockage) as well as relatively high flow.

As indicated by the decrease in run durations from C-16 (9.1h) to C-18 (3.2h), the amount of recovered recycle solvent decreased through the test sequence. This was due to a combination of factors including low conversion, sampling losses and excessive cracking in the hydrotreater.

Overall, this test sequence did not result in either a stable recycle regime or - except for C-16 - an acceptable overall conversion compared to batch test data.

4.3.1.2 Trench A Coal

Results of continuous liquefaction tests on Trench A coal without added catalyst are presented in Table 8. Initial runs in this sequence (C-9 and C-20) were with poorly hydrogenated solvent so results are of limited value with respect to conversion. However, these runs did provide liquid for solvent preparation for the recycle sequence:

C-22 A, B, C;	startup
C-23	first recycle
C-24	second recycle

Review of available data after C-24 (Table 8) suggested that conversion was stabilizing in the 75-80% range at feedrates of ~1.1 kg/h. This was considered to be unacceptable compared to the batch test data. Also there was an increasing shortfall in recycle hydrotreated solvent due to a combination of low conversion and high naphtha content of hydrotreater product.

Overall, it was considered that the test sequence confirmed that (reasonably) consistent conversion could be obtained in the liquefaction unit but that modification in equipment and/or process parameters would be required to duplicate batch test results.

4.3.2 Mechanical and Procedural Changes to the Continuous System

In view of the results - specifically low conversions - obtained in non-catalyzed continuous liquefaction test sequences, mechanical and procedural aspects of the continuous system were reviewed before starting the catalyzed test sequences (i.e., before Run C-25 (see Section 4.3.3)).

In tests to this point, it was observed that when the reactor was opened after a run, only 0.6 - 1 l of slurry was present despite a volume below the outlet tube of 1.7 l. This suggested mechanical transportation of slurry through the headspace; vapour removal alone would have resulted in very high solids concentrations which were not observed.

To reduce this (apparent) slurry entrainment, the impeller was changed from the 5 cm diameter, 3 blade, 45° pitch propeller to a 2.5 cm diameter, 90° pitch, 4 blade turbine. This was intended to reduce mixing intensity, thus reducing headspace gas re-entrainment and entrainment of slurry in gas flow. The reduction in impeller size allowed extension of the slurry feed inlet tube to within ~3 cm of the reactor bottom which was intended to give better feed mixing and reduce direct short circuiting.

During the same period, general streamlining of feed system tubing, valving, etc., was undertaken to reduce the incidence of blockage.

With respect to operating parameters, the set hydrogen gas flow was reduced to the minimum level (~200 l/h (NTP)) measurable

with the test equipment from previous levels of 400 - 500 l/h. This was all that could be done (short of extreme drying of coal) to reduce vapour phase flow.

Subsequent to these changes, the post run slurry volume retained in the reactor was consistently 1.1 l (±5%) which indicated an improvement as compared to previous slurry volumes as low as 0.6 l.

4.3.3 Liquefaction Tests with Ion Exchanged Iron Catalyst

Addition of iron by ion exchange[3] was selected for investigating iron catalysis. Also, modifications to the continuous unit were completed before starting tests on catalyzed liquefaction and some experience had been gained in operating the hydrotreater in an upflow mode. Iron uptake and contents of treated coals are presented in Table 9. Iron uptake by the procedure used was ~1% (vs dry coal) for coarse fractions of both Trench A and B coal samples. Only the coarse (i.e., partially beneficiated) fraction of ion exchanged coal was used in these tests. Representative proximate analyses (Tables 1 and 2) show the extent of ash rejection. Also, ion exchanged coarse coal samples were dried to 5-9 wt % moisture. Thus the slurry loading of inert material (moisture plus ash) was reduced by ~17% for both coal samples with a corresponding increase in coal organic feed at equivalent slurry solids content.

4.3.3.1 Trench B Coal

Results of the continuous liquefaction test sequence on ion exchanged Trench B coal are presented in Table 10.

With reference to the Table, the sequence of runs was:

C-25, C-26; startup
C-27; first recycle
C-28; second recycle
C-29; third recycle

The most striking feature of the results presented in Table 10 is the high and consistent conversion (89 - 92% by ash balance, 92 - 96% by calorific value). At these high conversion levels, the error in gravimetric conversion (due to mineral matter ignition weight losses being counted as volatile matter in the proximate analysis) becomes significant. Thus the calorific value conversions are systematically higher than weight-based conversion data.

There does not appear to be a significant trend in total conversion through the sequence of recycle runs, the differences are within the margin (roughly $\pm$2%) of experimental error.

The consistency of conversion values is particularly interesting in relation to solvent T:N ratios which varied in the range of 2.0 - 5.0 during the sequence. This observation is consistent with several possibilities including:

- donor capability of the solvent may not control conversion above some minimum level

- the iron catalyst allowed rehydrogenation of solvent during liquefaction.

Rehydrogenation in the reactor appears unlikely since the final T:N ratios were all in the 0.9 - 1.3 range. Thus it seems probable that donor capability of the solvent does not limit conversion in the solvent T:N range used, and also that available

solvent donor hydrogen is consumed (possibly in upgrading of primary products) beyond the consumption required for high conversion to THF soluble material.

Slurry feedrates were reasonably consistent (range 1.02 - 1.23 kg/h) in this test sequence. This rate corresponds to a mean residence time of ~1 h as compared to equivalent batch test conversions (Table 3) at 25 minute retention time. However, since the reactor is fully back mixed, the longer residence time can be considered as a correction factor for short circuiting.

Total measured gas phase products were 13% in runs C-28 and C-30, compared to tubing bomb gas yields of 15.9% at 25 minutes reaction time and 22.5% at 60 minutes reaction time (see Table 6). The difference is considered to be due to the fact that samples from the continuous system were taken at reactor pressure. Thus gas solubilities, particularly for C_2 - C_4 hydrocarbon diluted the actual gas yields.

Reflecting the increased operating experience, the "liquid + solid material balance" data (Table 10) indicate consistent high recovery (93 - 96 wt % = [wt product/wt feed] x 100). The indicated gas byproduct values (13% as daf coal) account for a further 2% of total feed, bringing overall recovery to the 95 - 98% range. Since determination of overall material balances was not a major project objective, accounting for 95 - 98% of feed material was considered adequate at the time when the tests were done. In retrospect, with the benefit of atmospheric gas samples from 60 minute tubing bomb tests, it seems likely that the consistent shortfall in material balance was due largely to undetermined gas byproduct. If it is assumed that gas yield from the continuous system at a 60 minute average retention time is roughly equivalent to that in an actual 60 minute tubing bomb test (see Table 6) the additional 6.7 wt % (vs daf coal) would

bring the overall content of feed accounted for to the 96-99% range.

From the discrepancy between tubing bomb and continuous system gas data, it is clear that the method of sampling the continuous unit will have to be changed to permit sampling of equilibrium 3 phase product with subsequent gas sampling at atmospheric pressure.

As for the previous test sequences, there was a decrease in solvent inventory through the sequence which resulted in reduced run durations. Material removed for sampling accounts for part of this loss, but the major loss was in in naphtha production. As discussed in Section 4.5, naphtha (removed by topping distillation before recycle) amounts to 14 - 16% of hydrotreated product from runs C-27 and C-28. This is (roughly) equivalent to 75% of daf coal feed.

With byproduct gas yields estimated from batch test data at 18.6 wt % (vs daf coal) the weight of material removed as gas and naphtha approaches 100% of the maf coal feed. Thus losses due to sampling and organic matter in the residue can account for net loss of solvent through the recycle sequence.

Overall, the test sequence on iron catalyzed Trench B coal was successful in demonstrating high conversions (equivalent to batch test data) which was the key project objective. Since the reactor changes were done immediately prior to this sequence, it is not possible to distinguish between effect of the catalyst and the system modification.

4.3.3.2 Trench A Coal

Results of the continuous iron catalyzed liquefaction test sequence on Trench A coal are presented in Table 11. Due to time

and budget constraints, this sequence was terminated after 3 runs:

C-29; startup
C-31; first recycle
C-32; second recycle

With reference to Table 11, conversion was uniformly high (91% by ash balance, 93 - 97% by calorific value), and slurry recoveries were in the 93 - 96 wt % range.

Measured byproduct gases from reactor pressure samples were in the 9-13% range which would bring material accountability up to the 95-98% range. If the atmospheric pressure tubing bomb gas data (Table 6) are used, a 60 minute reaction time would give ~22.5 wt % gas (vs daf coal). On a total material basis this adds a further 1.5% to recovery, bringing overall accountability up to the 96.5-99.5% range, exclusive of hydrogen.

Production of naphtha in hydrotreating of primary liquids from this test sequence (see Section 4.5) appears to show a downward trend which relates to the better recovery of solvent range material, resulting in only minor shortening of run duration (7.2 h to 5.9 h) through the 3 tests.

Overall, this test sequence is considered to confirm that high conversions can be obtained from Trench A coal in the continuous unit.

4.3.3.3 Effect of Iron as Catalyst and Additive

As noted above, modification to the agitator and slurry offtake of the continuous reactor were made before the series of runs using iron treated coal. Thus it is not possible to determine

whether addition of iron was beneficial with respect to coal conversion. Primary liquid quality was not monitored in these tests, so the effect (if any) of iron "catalyst" on this parameter cannot be documented either.

4.4 Projected Product Slate by Calorific Value

Using conversion and gas yield data from tubing bomb batch tests (with iron exchanged coal) and atmospheric pressure gas sampling, product slates in terms of calorific value have been calculated from Trench A and B coals at 25 and 60 minute reaction times (see Table 6). Results are presented in Tables 12 and 13.

Results are quite similar for both coal samples in that at 25 minutes reaction time, liquid yields (by difference) represent ~85% of coal calorific value while at 60 minutes reaction time, liquids represent ~75% of fuel calorific value. The difference (~10%) in both cases is due to increased hydrocarbon gas production, as total conversion for Trench A differed only slightly with increased reaction time. For Trench A, the difference (decrease of 0.6% by calorific value at 60 min.) was within experimental accuracy. For Trench B coal, the decrease (1.8% by calorific value) in conversion at 60 min vs 25 min reaction is significant but small. For both cases, the small decreases in total conversion could reasonably be attributed to coking in conjunction with gas evolution and (possibly) liquid upgrading.

The C^{+}_{5} liquid yields, although obtained by difference are considered to be realistically applicable to the continuous system since the overall material accountability for the continuous system (in the last test sequence on Trench A) was in the range of 96.5 - 99.5%. For the tubing bomb test, the product slates are considered fully reliable due to the closed nature of the test system.

4.5 Continuous Fixed Bed Hydrotreater

Summarized results of sixteen test runs on the fixed bed hydrotreater are presented in Table 14. This sequence of runs was completed without changing or reactivating the sulphidized Ni-Mo catalyst charge.

Representative axial reactor temperature profiles (Figures 4 - 6) show respectively the worst, best and (roughly) average temperature control obtained during the test sequence. From inspection of the Figures, even the best results operationally achieved (Figure 6, Run H-2) indicate temperature differences of $\pm$15-20 C° vs the set temperature. Since catalyst activity is quite strongly temperature dependent in the 275-350 C° range, the non-isothermal nature of the reactor is a complicating factor in assessing catalyst stability for separate test runs under the same nominal test conditions. However, larger axial temperature differentials (particularly on the high side) such as the +90 C° deviation vs set point in Run No. 1 were essentially eliminated by improved control due to operator experience. This eliminated the major problems of reactor coking and plugging which plagued previous downflow-type fixed bed configurations.

The reactor was opened once during the test period to remove a blockage due to fine catalyst at the upper (exit) end of the reactor which was presumably entrained into the constriction by upward flow of gas and liquid through the reactor. After removing the blockage, a glass wool plug was inserted ahead of the constriction and no further flow problems were observed.

For overall catalyst stability, results of Runs H-3 and H-16 (Table 14) can be compared. Creosote oil was treated at essentially the same space velocity and temperature set point in these runs. Full column temperature profiles were not taken for these

tests, but control was good, i.e., no major thermal excursions in either case. Catalyst age (as kg feed) was 12.7 at the start of Run 3 and 117 at the start of Run 16. These values correspond to ~6 and 57.3 g feed/g catalyst, which does not represent a long campaign in terms of commercial catalyst use. However, in terms of product tetralin:naphthalene ratio, Run H-16 (T:N=0.38) was at least equivalent to Run H-3 (product T:N=0.24). As previously noted, axial reactor temperature variations in the range of ±18 to 20C° preclude exact comparison of activity between runs. With this limitation, the data for Runs H-3 and H-16, appear to support an interpretation of at least equal catalyst activity.

Capillary GC analyses of raw creosote and products from Runs H3 and H16 are presented in Table 15. For what can be described as the naphtha fraction, i.e., material eluting up to and including trans-decalin, the data indicate a reduction in fraction of total peak area for the hydrotreated product. This may be misleading for two reasons. First, saturated alicyclics (particularly cyclohexane and methyl cyclohexane) elute before toluene and are not recorded. Second, the hydrotreating operation reduces the amount of non-distillable residue (see Figures 7 and 8), thereby increasing the amount of distillable heavy material and reducing the proportion of response due to naphtha since all results of Table 15 are expressed as a percentage of total GC detector response.

With respect to the hydrotreater runs on continuous system product, it should be noted that the "sludge" phase (recovered by ambient temperature centrifugation of THF/slurry residue, but insoluble at ambient temperature after THF removal) was not deliberately included in fixed bed hydrotreater feed. The project proposal, based on tubing bomb data similar to that presented in Table 3, anticipated that sludge would be included in hydrotreater feed for selected test sequences on the basis that it was treatable by a slurry catalyst system. The reason for not hydro-

treating the sludge fraction of the product was operational: it would not feed satisfactorily through the high pressure pump to the hydrotreater. Options considered for feeding sludge/liquid mix included installation of a pre-pressurizing pump on the hydrotreater system and heating the feed. (Note that the THF recovered material appears to be essentially all soluble in primary liquid during the topping distillation to remove THF and water; only when the topped product is cooled does the sludge phase separate.)

After the initial phase of non-catalytic liquefaction testwork it became reasonably clear that direct recyle of sludge to liquefaction resulted in acceptable conversion (of the sludge), so it was not considered worthwhile to modify the hydrotreater.

The hydrotreater runs on liquefaction products (Table 14) fall into two general categories: low feedrate (generally ~1.1 kg/hr) tests with high naphthalene conversions and relatively high feedrate (1.4 - 1.95 kg/hr) tests with correspondingly lower naphthalene conversions. The latter sequence corresponds to the treatment of products from Fe-exchanged catalyzed liquefaction in which high coal conversions were uniformly observed. Also in this sequence, hydrogen flowrate was held at the lowest controllable level in an attempt to slow the vapour phase and (hypothetical) foam phase transport of feed through the reactor. In the earlier sequence, lower liquid feedrate was used to obtain maximum concentrations of donor species which were assumed to be necessary for high coal conversion.

As previously noted, the changeover to catalytic liquefaction tests took place after changes to the liquefaction reactor agitator, feed geometry and hydrogen flowrate. Effects of these changes cannot be separately evaluated with present data.

With respect to general hydrotreater performance, the summarized results of Table 15 and specific naphthalene conversion data (Table 16) indicate that the fixed bed system can be controlled to produce a desired proportion of hydroaromatics (e.g,. tetralin) subject to kinetics of following saturation reactions such as:

$$\text{tetralin} + 2H_2 \xrightarrow{\text{catalyst}} \text{decalin (non donor alicyclic)}$$

4.5.1 Distillation Behaviour of Hydrotreater Products

Table 17 presents data on the naphtha fraction of hydrotreater products; Figures 7 and 8 show TGA distillation curves of raw and hydrotreated creosote oil (Run H-16).

The naphtha (ibp-200°C) fraction is of most interest, since it represents net product. In non-catalyzed runs (H6 and 7, Table 17), hydrotreating resulted in excessive naphtha - i.e., greater than the actual coal conversion - which accounts for the need for make-up solvent in corresponding continuous liquefaction test series. For the iron catalyzed liquefaction feedstocks (H12-15, Table 17), it would appear that naphtha - as defined - represents roughly 50 - 75% of the weight of the daf coal feed. This result, while subject to some uncertainty, suggests that hydrotreating conditions (i.e., treatment to lower T:N ratios) did not result in excessive over-cracking of solvent for Trench B coal. The third cycle hydrotreated product (H13) indicates that overall naphtha yield (75% of daf coal) represents a large fraction of total conversion (90%, daf, Table 10). Further work is required to determine whether this high naphtha yield could be sustained while maintaining an adequate amount of recycle solvent. For iron exchanged Trench A coal, results of H-14 and H-15 suggest a trend to lower naphtha yield due to recycle, but further experimental confirmation is required.

4.5.2 Elemental Analyses

Table 18 presents elemental analyses of hydrotreater feed and product samples for second cycle Fe exchanged Trench A and B liquefaction tests. For hydrogen, the indicated increases (+0.7% and 0.8% absolute, +8% and +9% relative) are consistent with hydroaromatic formation. Oxygen reductions (63% and 49%, relative) are incomplete, which is consistent with capillary GC data indicating residual phenols in hydrotreater product (Table 15). Nitrogen reductions (26% and 43% relative) are low, as expected for the low severity of hydrotreatment and known refractory nature of nitrogen heterocycles toward removal by hydrotreatment. Accurate determination of sulphur removal will require an analytical procedure with a lower detection limit.

The elemental analysis data suggest a hydrogen consumption of 1-1.3 wt % for the entire liquid. It is not considered realistic to attempt a detailed calculation of how this hydrogen consumption relates to coal fuel. Qualitatively, however, a 1.3% consumption on total liquid using a 2:1 solvent/coal ratio and Trench A coal (daf content ~60%) would correspond to a 4.3 wt % hydrogen consumption of daf coal. Hydrogen consumption from tubing bomb tests is ~1.4% for Trench A coal. On this basis, the approximate worst case for global hydrogen consumption appears to be ~5.7 wt % of daf coal for Trench A coal.

4.5.3 Gas Byproduct from Hydrotreater

Useful gas byproduct data from the hydrotreater were not obtained due to hydrogen dilution in the (batch) product receiver.

Liquid recoveries of 97 - 99% (Table 12) suggest that C_1-C_4 yields were low, but further testwork, possibly using the tubing

bomb approach as decribed in Section 4.2.2 will be necessary to determine byproduct gases.

The tubing bomb approach would (roughly) model industrial scale ebullated bed hydrotreating which might be more realistic than projections based on fixed bed work. However, for continuation of continuous system work on Hat Creek coal it will also be necessary to modify the hydrotreater exhaust system to allow sampling of equilibrium gas plus liquid products.

4.5.4 Nuclear Magnetic Resonance (NMR) Analyses of Hydrotreater Feed and Product

Data from ^{1}H-NMR analyses on hydrotreater feed and product samples are presented in Table 19. These limited data suggest that (NMR indicated) aliphatic hydrogen must come from substantial amounts of aliphatic side chains, since the hydroaromatic contents of feed and products (Table 13) would not be sufficient to provide the indicated H_{al}:H_{ar} ratios. Qualitatively, however, the increases in aliphatic:aromatic ratios are consistent with hydroaromatic formation and cracking.

4.5.5 Hypothetical Transport and Temperature Control Mechanisms in Upflow Fixed Bed Hydrotreating

The conventional petroleum industry approach to fixed bed hydrotreatment of heavy liquids, especially those containing a non-distillable fraction, is to use a co-current (gas and liquid) downflow reactor. In this case, gravity flow ensures that non-vaporized liquid will eventually report to the reactor outlet. Earlier configurations of the B.C. Research test system were operated in a downflow mode, and temperature control was uniformly difficult, leading to frequent coking of catalyst and finally total blockage. This was attributed to rapid, exothermic

reaction resulting in a sharp spike in the axial temperature profile similar to but larger and sharper than the (upward) deviation shown in Figure 5 (first furnace zone). A similar profile was observed in a downflow pilot reactor operated by Veba Oehl Gmbh. Subsequent discussions with Dr. J.J. Starzomski (Nova Scotia Research Foundation) revealed that he had overcome a similar problem by operating an anthracene oil hydrotreater in a co-current upflow mode. This conversion was made to the B.C. Research unit in September, 1983, and subsequent operation (subject to careful monitoring) has been relatively smooth.

Both creosote oil (feed for startup solvent) and primary liquefaction products contain appreciable quantities of non-distillable residue (see Figure 7). Thus, an accumulation of liquid at the bottom of the unit was anticipated. However, opening of the bottom drain of the reactor after early test runs recovered only small (0.3 - 0.8 l) amounts of liquid which did not contain a disporportionate amount of high boiling or non-distillable material.

Also, on initial consideration, there appeared to be no obvious reason why exothermic reactions should not cause temperature deviations in an upflow reactor.

One hypothetical explanation of these phenomena (i.e., pitch transport through the reaction zone and relative lack of temperature deviations) is upward transport of pitch as a foam or mist. This could provide a temperature buffer on highly exothermic reactor zones, as well as a transport mechanism for the minor amount of nondistillable material in hydrotreater product (Figure 8). This mode of upward transport would result in a fluid downflow or reflux of nondistillables due to the foam collapse (or mist trapping on solid surfaces) which would be a buffer on exothermic reaction zones.

The "foam" hypothesis for transport/reflux is preferred on the basis of the strong foaming tendency of both primary and hydrotreated coal liquids. The foaming tendency is observed during depressurization of receivers; too-rapid depressurization can easily result in overflow of thick, relatively stable foams.

While this discussion is hypothetical, it is considered to have potentially important implications for use of scaled up fixed bed systems. Inherent control of temperature by foam transport/reflux in a upflow reactor would, conceptually at least, be much simpler than expedients such as excessive hydrogen dilution, product recycle or cooling which might be required for a conventional downflow reactor.

For large scale operation, ebulliated bed hydrotreating sytstems (e.g., "H-Oil" and "LC Fining" processes) would eliminate thermal gradient problems as well as allowing on-line catalyst replacement. However, ebulliated bed systems are more complex than fixed beds, and it would be of interest to compare capital and operating costs for ebulliated bed vs upflow fixed bed reactors.

4.6 Beneficiation of Hat Creek Coal

Although beneficiation of Hat Creek coal before liquefaction was not an original objective of the project, it was observed that the process of iron ion exchange for catalytic tests resulted in segregation of mineral matter (ash) in the fine, very slow settling fraction of treated material (see Table 1).

Conventional washing of Hat Creek Trench A material [7] in the 600 x 150 micron size range (28 x 100 mesh) has been shown to produce a clean coal with 26.1% ash (dry basis) and a reject fraction with 58% ash at a combustible recovery to clean coal of 72%. Better effectiveness and cleaner coal fractions (minimum

20.3% ash, dry basis) were obtained on other raw coal size fractions.

The ion exchange procedure was done on hammermilled - 150 micron (-100 mesh) coal which had not been beneficiated. Table 20 presents data from a water only cyclone test on 600 x 150 micron Trench A coal under optimized conditions, and results of Trench A and B ion exchange tests which were not optimized as the decantation of fines was terminated arbitrarily at a point where the residue ("coarse" or clean coal) was sufficiently settled for transfer to drying trays.

The tabulated data show better performance for the water only cyclone, as would be expected for an optimized procedure. However, it would be of very considerable interest to determine whether coal washed at coarser sizes to the 20 - 26.1% ash contents range [7] could be further beneficiated by an optimized procedure after grinding to -150 microns. Considering that ash rejection is mainly as fine clay and that liberation (i.e., separation of mineral and coal components) is likely to improve with finer grinding, there appears to be a potential for physical cleaning of Hat Creek coal to dry basis ash levels below 20%. This would be very desirable in relation to liquefaction, since the inert mineral matter (28 - 47%) in dry run of mine coal is a significant factor in sizing of process equipment and particularly in separation of primary liquid from residue.

4.7 Economic Analysis

Although the results presented in this report do not entirely define either a specific process or costs for liquefaction of Hat Creek coal, it is of interest to make a preliminary analysis of costs and revenues to determine whether the prospect of commercial application is realistic.

Data presented in Table 21 for Trench A coal (highest ash feed) are based on the following assumptions:

- run of mine coal ($10/tonne or approximately $1/GJ) can be cleaned to 28.8% ash at 75% combustibles recovery - i.e., the result obtained in the Fe exchange test. (This is considered to be realistic in view of optimized washing-test recovery[7] of 73% combustibles at 26% ash in clean coal.)

- cleaning (water only cyclones) and drying costs of $4/net tonne clean coal (exclusive of fuel which is reject coal at 62% ash, dry basis)

- all C_1 - C_4 product gases used for reforming and plant fuel (full use for reforming would generate hydrogen equivalent to ~4 g hydrogen/100 g daf coal which is somewhat less than the worst case hydrogen consumption (see above, section 4.5.2) of 5.7 g/100g daf. However, C_1-C_4 gases from the hydrotreater would probably be sufficient to balance this (worst case) shortfall.

- light syncrude product is valued at the current world price of Cdn $36/barrel (~ U.S. $27/barrel).

With this set of assumptions, total material costs are estimated at $22/tonne of clean coal processed and revenue is $67.30/tonne of clean coal processed.

The material cost per barrel of oil product is Cdn $11.76, and the ratio of revenue:raw material costs is 3.06. As a rule of thumb, a projected revenue:material costs ratio of 2.0 is sufficient to support a manufacturing or processing operation of reasonable complexity. Due to the large recycle component in coal liquefaction, the process can be considered to be of much

more than average complexity. However, the ratio of 3.06 is also well above the rule of thumb minimum.

If C_2-C_4 products (8.5% of product calorific value) are economically valued at parity with syncrude for feedstock, and purchased natural gas at $3/GJ (i.e., marginally below the current export price) is used for reformer feed and process heat, there is an 5.8% increase in gross revenue bringing the revenue:material cost ratio to 3.24. Similarly, if the naphtha product could be chemically treated for removal of phenol and (basic) nitrogen components, the upgraded product could be marketed as motor gasoline blendstock at a premium of ~20% over light crude oil. This would increase the revenue: material cost ratio to 3.85.

5.0 CONCLUSIONS

Major conclusions from the study are considered to be as follows:

1. Using donor solvent methodology, direct liquefaction of Hat Creek coal gives high ($\geq$90%) total conversion in a single stage back mixed continuous system.

2. Primary liquid product can be hydrotreated to generate naphtha (net product) and a satisfactory recycle donnor solvent using a continuous fixed bed catalytic hydrotreater.

3. Under conditions tested, net liquid product is largely naphtha (C_5 - 200°C) at a yield of 75($\pm$2)% compared to the calorific value of feed coal.

4. Under conditions tested, gas byproducts of the continuous liquefaction/hydrotreating operation (CO and C_1-C_4 hydrocarbon gases) represent 14-17% of the calorific value of feed coal. These gas products are (marginally) adequate to provide, by reforming, the hydrogen required for liquefaction and hydrotreating.

5. The sludge or "bottoms" fraction of tetrahydrofuran soluble primary liquid product can be recycled to liquefaction without affecting the conversion ($\geq$90%) of feed coal - i.e., "bottoms" are effectively converted by recycle.

6. Preliminary economic analysis based on test data and current hydrocarbon prices indicates that direct liquefaction of Hat Creek coal is potentially viable.

Secondary conclusions from the data are:

- beneficiation of fine (-150 μ) Hat Creek coal can be obtained by selective sedimentation and improved by using ferrous sulphate as a dispersant.

- commercial pelleted NiMo hydrotreating catalyst is stable (i.e., retains its hydrogenation activity) in fixed bed operation on primary coal derived liquid provided temperature control is adequate.

- upflow operation of a lab scale fixed bed hydrotreater results in substantially improved temperature control compared to downflow.

Items not resolved by results to date include:

- the effect of iron catalyst on liquefaction yield and primary product quality.

- C_1-C_4 gas byproduct yields from hydrotreating.

- quantitative hydrogen consumption in hydrotreating.

6.0 RECOMMENDATIONS

For further studies on direct liquefaction of Hat Creek coal, the following areas are recommended for experimental effort:

1. Accurate mass balances and hydrogen consumption data for the continuous systems. (This will require modifications to allow sampling of equilibrium products).

2. Variation of hydrotreating conditions to determine gas, naphtha and +200°C products vs severity.

3. Investigation of separating alicyclic (non-donor) components of the +200°C recycle donor solvent.

4. Assessment of the stability of tetrahydrofuran for use (with quantitative recycle) as a separation solvent.

In view of the favourable technical results obtained to date, items such as environmental stability of waste should also be addressed in future work to allow a more general assessment of direct liquefaction as applied to Hat Creek coal.

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TABLE 1

PROXIMATE ANALYSES OF HAT CREEK "TRENCH A" SAMPLES

Subsample Code	As Tested (wt%)				Dry Basis (wt%)			Dry, Ash Free (wt %)	
	Moisture	Volatile Matter	Fixed Carbon	Ash	Volatile Matter	Fixed Carbon	Ash	Volatile Matter	Fixed Carbon
B-01-2	18.71	24.18	17.69	38.81	29.75	22.51	47.74	56.93	43.07
B-01-3	18.85	26.84	15.02	39.01	33.07	18.51	48.07	63.68	36.31
B-01-4	18.23	25.38	17.80	38.18	31.04	22.27	46.69	58.23	41.77
C-01-2	22.53	24.57	17.77	34.53	31.71	23.71	44.57	57.21	42.79
C-02-2	20.31	24.04	17.67	37.53	30.17	22.76	47.09	57.02	42.98
C-03-1	22.15	24.17	19.41	33.80	31.05	25.54	43.42	54.88	45.12
Fe-Exchgd C-03-01, coarse	7.92	32.64	30.58	28.78	35.45	33.30	31.26	51.57	48.43
Fe-Exchgd C-03-1, fine	5.07	24.71	11.52	58.62	26.03	12.22	61.75	68.05	31.95

TABLE 2

PROXIMATE ANALYSES OF HAT CREEK "TRENCH B" SAMPLES

Subsample Code	As Tested (wt%)				Dry Basis (wt%)			Dry, Ash Free (wt %)	
	Moisture	Volatile Matter	Fixed Carbon	Ash	Volatile Matter	Fixed Carbon	Ash	Volatile Matter	Fixed Carbon
B-01-2	19.20	29.79	27.84	22.66	38.87	35.09	28.04	34.02	45.98
B-01-3	19.17	30.26	27.49	22.51	37.44	34.71	27.85	51.89	48.11
B-01-4	18.33	28.37	29.76	23.14	34.74	36.93	28.33	48.47	51.53
B-01-5	19.83	31.68	25.24	22.91	39.52	31.91	28.58	55.33	44.67
C-02-2	20.59	28.21	25.57	25.06	35.52	32.92	31.56	51.89	48.10
C-03-2	20.44	27.63	23.26	28.02	34.73	30.05	35.22	53.61	46.39
C-03-2, coarse	8.77	31.14	30.97	28.99	34.13	34.09	31.78	50.03	49.97
C-03-2, fine	6.13	32.78	18.31	42.68	34.92	19.61	45.47	64.04	35.96
Fe-Exchgd C-03-2, coarse	9.09	33.13	33.78	23.81	36.44	37.37	26.19	49.37	50.63
Fe-Exchgd C-03-2, fine	8.45	26.28	16.42	48.51	28.71	18.31	52.99	61.07	38.93

TABLE 3

RESULTS OF LOCKED CYCLE TUBING BOMB EXPERIMENTS(1)

RUN	RECYCLE	T/N		CONVERSION (wt% daf)	+525° NON-DISTILLABLE (wt% of liquid)	GAS DATA (wt% daf)	
		Initial	Final			Gas Product	H_2 Consumption
465/4	Startup	0.12	0.02	55.4	11.6	16.4	1.2
461/4	1	1.14	0.39	88.6	9.6	13.0	0.9
463/4	2	1.92	0.43	89.4	10.0	11.3	0.7
468/4	3	3.20	1.00	90.0	7.0	11.2	0.9

(1) Conditions: T=440°C, reaction time = 25 min, initial P_{H_2}=5.5 MPa, solvent:Coal=3.

Startup solvent was creosote oil; hydrotreated recycle (see Table 4) solvent used in cycles 1-3.

TABLE 4

RESULTS OF LOCKED CYCLE TUBING BOMB CATALYTIC HYDROGENATION TESTS[1] ON THF EXTRACTS FROM HAT CREEK COAL LIQUEFACTION

Bomb No.	Hydrogenation Test Data					
	Tetralin: Naphthalene		+525°C Residue		Catalyst	
	Initial	Final	Initial	Final	wt % Recovered	Age (final) (g liquid/g catalyst)
455/4	0.02	1.14	14.6	2.1	99	20
461/4	0.39	1.92	9.6	0.8	98.5	40
463/4	0.43	3.20	10.0	0.6	102	60

(1) Conditions: T=375°, Reaction Pressure = 14 MPa (maintained), reaction time = 60 min., initial catalyst (per bomb) 1.75 g sulphidized Ni-Mo. Feed for each test was ambient temperature THF extract (topped to 120°C for solvent and water removal) from tubing bomb liquefaction tests with Trench B coal.

TABLE 5

RESULTS OF ATMOSPHERIC PRESSURE GAS SAMPLE ANALYSES FOR TUBING BOMB TESTS[1] WITH IRON CATALYST

Bomb No.	Sample	Byproduct Gases (wt% daf coal)						
		CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO	CO_2	Total
535/1[2]	C-28 feed slurry (Trench B, iron catalyzed)	3.4	2.2	1.0	0.1	1.5	10.8	19
535/2[3]	C-28 feed slurry (Trench B, iron catalyzed)	2.7	3.9	0.8	-	1.3	14.1	22.9
	Mean values	3.0	3.0	0.9	0.05	1.4	12.4	21
536/1[4]	C-29 Feed slurry, (Trench A, iron catalyzed)	3.6	5.8	1.3	0.2	1.7	20.0	32.6
536/2[5]	C-29 Feed slurry, (Trench A, iron catalyzed)	3.7	5.0	1.2	0.2	1.7	21.8	33.6
	Mean values	3.6	5.4	1.2	0.2	1.7	20.9	33.2

(1) 440°C, 25 minutes, P~10MPa
(2) Conversion (ash balance) 88.9%
(3) Conversion (ash balance) 84.2%
(4) Conversion (ash balance) 84.7%
(5) Conversion (ash balance) 87.8%

TABLE 6

RESULTS OF ATMOSPHERIC PRESSURE GAS SAMPLE ANALYSES
FOR 25 AND 60 MINUTE TUBING BOMB TESTS(1)

COAL SAMPLE	REACTION TIME (min)	TOTAL CONVERSIONS (%)			GAS YIELDS (%, daf)							
		Gravimetric	Ash Balance	Calorific Value	CO	CO_2	CH_4	C_2H_6	C_3H_8	iC_4H_{10}	C_4H_{10}	Total
Trench A	25	89.5	87.4	91.0	0.9	11.9	1.9	1.1	0.17	0.01	0.03	15.9
	60	89.8	87.2	90.4	0.9	12.8	3.8	2.4	1.6	0.17	0.48	22.5
Trench B	25	91.2	91.1	93.3	0.8	8.95	1.8	0.96	0.27	0.02	0.06	12.9
	60	90.0	89.8	91.5	0.8	9.73	3.5	2.1	1.5	0.15	0.43	18.6

(1) Conditions: T=440°C, initial P_{H_2}=6.9 MPa, solvent (hydrogenated creosote)/coal=2

TABLE 7

SUMMARIZED DATA FOR UNCATALYZED CONTINUOUS TESTS ON HAT CREEK TRENCH B COAL

Run No.	Solvent	Tetralin: Napthalene		Slurry Feedrate (kg/h)	Run Duration (h)	Conversion (Ash Balance, wt%, daf)	Gas Product (wt% daf)
		initial	final				
C-7	Startup mix(2)	0.05	ND(3)	0.99	7.1	52.3	ND
C-8	Startup mix(2)	0.05	ND	1.09	6.0	67.4	ND
C-10	C-7 + C-8	0.08	0.04	1.52	7.0	51.3	ND
C-11	Startup mix(2)	0.05	ND	1.45	5.9	44.12	6.6
C-12	Hydrotreated Creosote	0.64	ND	0.96	6.6	57.9	7.9
C-13	Hydrotreated C-10	0.79	0.23	1.24	6.4	76.2	7.3
C-16	Hydrotreated C-11 + C-12	0.83	0.56	0.77	9.1	86.7	7.6
C-17	Hydrotreated C-16	2.65	0.23	1.40	5.75	74.3	5.2
C-18	Hydrotreated C-17	0.76	0.25	1.36	3.2	63.1	ND

(1) Conditions: C-7 through C-12: T=400°C, P=14MPa, acetone used as workup solvent.
C-13 through C-18: T=440°C, P=14MPa, THF used as workup solvent.

(2) Hydrotreated 2:1 mixture of creosote oil and anthracene oil.

(3) ND = not determined.

TABLE 8

SUMMARIZED DATA FOR UNCATALYZED CONTINUOUS TESTS ON HAT CREEK TRENCH A COAL[1]

Run No.	Solvent	Tetralin: Napthalene		Slurry		Run Duration (h)	Conversion[2] (Ash Balance) (wt%, daf)	Gas Product (wt% daf)
		Initial	Final	Solids Content (wt%)	Feedrate (kg/h)			
C-9	non-hydrogenated, +200°C Creosote	0.015	ND	24.0	1.29	6.83	59	ND
C-20	hydrotreated anthracene oil	0.37	ND	26.8	0.52	8.25	63	ND
C-22A	H-4 + H-3 product	2.53	ND	27.6	1.59	3.28	53	5
C-22B	H-4 + H-3 product	2.53	ND	27.6	0.61	2.17	ND	ND
C-22C[3]	C-22 A + B product	1.15	ND	ND	2.1	2.33	69[3]	ND
C-23	H-5 + H-1[4] product	1.36	ND	26.8	1.08	10.67	77	7
C-24	H-6 + H-3[4] product	1.04	ND	28.6	1.14	8.33	78	ND

(1) Conditions: T=440°C, P=14MPa (except C-9: T=400°C and C-20, P=5 MPa autogenous pressure.)

(2) By THF extraction, ambient temperature

(3) Part of C-22 A + B product recycled directly

(4) Topped hydrotreated creosote (H-1 and H-3 products) added to make up shortfall of topped recycle liquid.

TABLE 9

IRON CONTENTS AND UPTAKE OF HAT CREEK
COAL SAMPLES AFTER ION EXCHANGE

	Fe Content (wt% dry coal)	Fe Uptake (wt% dry coal)
Hat Creek Tr A C-03-2	1.604	-
Hat Creek Tr A Fe-Exchanged C-03-2, Coarse	2.649	1.05
Hat Creek Tr A Fe-Exchanged, C-03-2, Fine	3.138	1.53
Hat Creek Tr B C-03-2	1.119	-
Hat Creek Tr B Fe-Exchanged, C-03-2, Coarse	2.337	1.22
Hat Creek Tr B Fe-Exchanged, C-03-2, Fine	2.855	1.74

TABLE 10

SUMMARIZED DATA FOR IRON CATALYZED CONTINUOUS TESTS ON TRENCH B COAL(1)

Run No.	Solvent(2)	Tetralin: Napthalene		Slurry		Run Duration (h)	Conversion		Gas Product (wt% daf)	Liquid Solid Material Balance %
		Initial	Final	Solids Component (wt %)	Feedrate (kg/h)		Ash Balance (wt%, daf)	Calorific Value (%)		
C-25	H-8/H-9/H-10	3.4	Avg. 1.02	32.4	1.23	6.25	89	92	ND	ND
C-26	H-8/H-9/H-10	2.0		28.4	1.10	5.67	91	92	ND	94
C-27	H-11	2.2	0.9	29.1	1.03	12.48	90	92	ND	93
C-28	H-12	5.0	1.3	34.3	1.02	8.62	92	96	13	93
C-30	H-13	3.8	ND	29.2	1.18	5.72	92	95	13	96

(1) Conditions: T = 440°, P = 14 MPa, THF used as workup solvent.
(2) All solvents hydrotreated and topped to 200°C.
ND = Not Determined.

TABLE 11

SUMMARIZED DATA FOR IRON CATALYZED CONTINUOUS TESTS ON TRENCH A COAL(1)

Run No.	Solvent	Tetralin: Napthalene		Slurry		Run Duration (h)	Conversion		Gas Product (wt% daf)	Liquid + Solid Material Balance %
		initial	final	Solids Component (wt%)	Feedrate (kg/h)		Ash Balance (wt%, daf)	Calorific Value (%)		
C-29	H-8/H-9/H-10	5.8	1.6	34.5	1.11	7.17	91	97	12	95
C-31	H-14	4.6	1.4	33.0	1.05	6.75	91	94	9	96
C-32	H-15	4.4	N/D	32.5	1.15	5.93	91	93	13	93

(1) Conditions: T = 440°, P = 14 MPa, THF used as workup solvent.
(2) All solvents hydrotreated and topped to 200°C.
ND = Not Determined.

TABLE 12

TRENCH A COAL - PRODUCT SLATES BY CALORIFIC VALUE FOR 25 AND 60 MIN BATCH TESTS[1]

	% OF FEED COAL CALORIFIC VALUE	
	25 min Reaction	60 min Reaction
Coal (16.3 GJ/tonne)	100	100
Residue	9.0	9.6
CH_4	3.9	7.6
C_2H_6	2.0	4.4
C_3H_8	0.31	2.9
(n,i) C_4H_{10}	0.07	1.2
CO	0.3	0.3
(subtotal gases)	(6.58)	(16.4)
C_5+ liquids (by difference)	84.4	74.0

(1) Fe exchanged coal, hydrogenated creosote (+200°C) solvent, coal to solvent ratio 1:2, 440°C, initial P_{H_2} 6.9 MPa, see Table 6.

TABLE 13

TRENCH B COAL - PRODUCT SLATES BY CALORIFIC VALUE FOR 25 AND 60 MIN BATCH TESTS(1)

	% OF FEED COAL CALORIFIC VALUE	
	25 min Reaction	60 min Reaction
Coal (17.9 GJ/tonne)	100	100
Residue	6.7	8.5
CH_4	3.7	7.2
C_2H_6	1.8	4.0
C_3H_8	0.51	2.7
(n,i) C_4H_{10}	0.15	1.1
CO	0.29	0.3
(subtotal gases)	(6.55)	(15.3)
C_5+ liquids (by difference)	86.5	76.2

(1) Fe exchanged coal, hydrogenated creosote (+200°C) solvent, coal to solvent ratio 1:2), 440°C, initial P_{H_2} 6.9 MPa, see Table 6.

TABLE 14

SUMMARY OF CONTINUOUS HYDROTREATER[1] OPERATIONS

Run No.	Feed	Feed Rate (kg/h)	Set Temp. (°C)	WHSV[2] (kg/h/kg)	H_2 Rate[3] (sl/h)	Duration (h)	Tetralin: Napthalene[4]				Cumulative Catalyst Age	
							Initial	Final	In +200°C Fraction	Liquid Recovery (%)	Time[6] (h)	Feed Weight (kg)
H1	Creosote	0.91	325[5]	0.45	300	7.0	0.015	29.9	ND	ND	7.0	6.37
H2	Creosote	1.2	300	0.59	300	5.25	0.015	2.6	ND	ND	12.25	12.67
H3	Creosote	3.2	300	1.57	300	5.0	0.0	0.24	ND	ND	17.25	28.67
H4	C9 + C20	1.1	300	0.54	300	3.0	0.09	3.47	ND	ND	20.25	31.97
H5	C22	1.1	325	0.54	300	3.42	0.9	22.3	ND	ND	23.83	35.91
H6	C23	1.1	325	0.54	erratic	6.33	0.8	22.3	20.81	98	30.17	42.88
H7	C24	0.79	325	0.39	300	1.33	ND	ND	ND	ND	31.50	43.93
		1.37	325	0.67	300	3.33	0.40	9.08	7.91	100	34.83	48.50
H8	Creosote	1.3	325	0.64	in spurts	8.42	0.015	8.4	ND	ND	43.25	59.51
H9	Creosote	1.2	325	0.59	400	11.83	0.015	ND	ND	ND	56.08	73.71
H10	Creosote	1.2	325	0.59	400	7.0	0.015	ND	ND	ND	63.08	82.11
H11	C25 + C26	1.95	325	0.96	200	5.25	1.02	2.50	2.23	ND	68.33	92.34
H12	C27	1.84	325	0.90	250	5.05	0.9	ND	6.82	98	73.42	101.70
H13	C28	1.91	325	0.94	200	2.83	1.3	5.83	ND	100	76.25	107.12
H14	C29	1.76	325	0.86	200	3.07	1.6	5.91	ND	99	76.32	112.63
H15	C31	1.44	325	0.71	200	3.0	1.37	ND	8.46	99	82.33	116.95
16	Creosote	3.14	300	1.54	300	4.33	0.015	0.38	ND	ND	86.67	130.56

(1) Hydrotreatment carried out on sulphided American Cyanamid Aero HDS-3A Ni-Mo catalyst at 14MPa total pressure; weight of catalyst in hydrotreater: 2040 g.

(2) Weight hourly space velocity WHSV = $\frac{\text{Feed Rate (kg/hr)}}{\text{Weight of catalyst (kg)}}$

(3) Hydrogen feed rate is approximate; sl/hr = Standard litres per hour.

(4) Tetralin: Naphthalene ratio.

(5) Large temperature deviations (up to 415°C).

(6) Cumulative time; does not include heat-up and cool-down periods.

ND = not determined.

TABLE 15

CAPILLARY GC ANALYSES OF CREOSOTE AND HYDROTREATER PRODUCTS FOR CATALYST STABILITY TEST, RUNS H-3 and H-16

Component	Raw Creosote	Composition (% peak area) Hydrotreater Product	
		H-3	H-16
toluene	0.79	1.18	0.95
m+p-xylene	2.85	3.09	2.80
o-xylene	1.47	1.59	1.45
trimethyl benzene	1.51	1.93	1.46
phenol	2.22	1.54	1.09
indan	17.4	17.8	17.60
cis-decalin	0.39	0.51	0.53
m+p cresol	0.80	0.63	0.72
trans decalin	0.09	0.51	0.19
Subtotal all peaks up to/including trans decalin	41.7 (25 peaks)	39.2 (31 peaks)	38.0 (34 peaks)
tetralin	0.36	4.5	6.54
naphthalene	23.3	18.6	17.0
Subtotal T+N	23.4	23.1	23.5
9, 10 dihydrophenanthrene	0.17	0.82	0.55
phenanthrene	4.14	3.28	3.01
anthracene	1.06	0.10	0.22
pyrene	1.58	0.94	1.18

TABLE 16

HYDROTREATER NAPHTHALENE CONVERSIONS

Run No.	Set Temperature (°C)	Feedrate (kg/h)	WHSV (kg/h/kg catalyst)	H_2 (sL/h)	Naphthalene (%)			Tetralin (%)		Decalin (%)	
					feed	product	conversion(1)	Feed	Product	Feed	Product
H-4	300	1.1	0.54	300	10.94	3.59	67.0	0.94	12.46	0.47	1.08
H-5	325	1.1	0.54	300	9.36	ND	ND	8.84	ND	ND	ND
H-6	325	1.1	0.54	erratic	9.27	0.7	92.5	7.42	15.58	1.25	4.27
H-11	325	1.95	0.96	200	7.75	4.47	42.4	7.92	11.17	1.47	1.54
H-13	325	1.91	0.94	200	5.31	1.63	69.3	7.39	9.52	1.62	1.51

(1) Percent naphthalene conversion determined from % naphthalene in feed and in product.

TABLE 17

TOPPING DISTILLATION DATA FOR
HYDROTREATER PRODUCTS

Run No.	Feed	Products (wt%)		Naphtha (ibp-200) as % daf coal	Notes
		ibp-200°C	+200°C		
H-6	C-23 product	24(1)	76	>100	Third Cycle, Trench A Non-catalyzed
H-7	C-24 product	24	76	>100	Fourth Cycle, Trench B Non-catalyzed
H-8	Creosote	30	70	NA(2)	
H-12	C-27 product	14	86	70(±10)	Second cycle, Trench B Fe exchanged
H-13	C-28 product	16	84	75(±10)	Third cycle, Trench B Fe exchanged
H-14	C-29 product	15	85	75(±10)	First cycle, Trench A Fe exchanged
H-15	C-31 product	12	88	60(±10)	Second cycle, Trench A Fe exchanged

(1) ibp - 105 (water cut) 0.6%
105 - 165 4.1
165 - 180 6.2
180 - 200 13.1
24.0

(2) Not applicable.

TABLE 18

ELEMENTAL ANALYSES(1) OF HYDROTREATER FEED AND PRODUCT SAMPLES

Sample	Elemental Analysis (wt%) C	H	N	O(2)	S	% Change(3) C	H	N	O	S	Notes
C-27 product	88.56	8.85	0.39	1.89	0.31	--------- NA ----------					Trench B, Fe exchanged, second cycle.
H-12 product	89.42	9.58	0.29	0.70	0.2	+1	+8	-26	-63	-(>35)	
C-31 product	88.16	8.81	0.44	2.37	0.22	--------- NA ----------					Trench A, Fe exchanged, second cycle.
H-15 product	89.95	9.58	0.25	1.20	0.2	+2	+9	-43	-49	-(>10)	

(1) Canadian Microanalytical Ltd.

(2) O by difference.

(3) $\frac{\text{wt\% in product - wt\% feed}}{\text{wt\% in feed}}$

TABLE 19

ALIPHATIC/AROMATIC HYDROGEN RATIOS (H_{al}/H_{ar})
FOR HYDROTREATER FEED AND PRODUCT SAMPLES

Sample	H_{al}:H_{ar}	Notes
C-27 product	2.72	Trench B, Fe exchanged, second cycle
H-12	4.79	Hydrotreated C-27
C-31 product	3.02	Trench A, Fe exchanged, second cycle
H-15	5.25	Hydrotreated C-31

TABLE 20

BENEFICIATION DATA ON HAT CREEK COAL

	Water Only Cyclone[1] (Trench A Coal)	Fe Ion Exchange & Decantation	
		Trench A Coal	Trench B Coal
Feed Ash (wt%, dry)	40.6	43.4	35.2
Clean Coal Ash (wt%, dry)	26.1	31.3	26.2
Refuse Ash (wt%, dry)	72.9	61.8	53.0

(1) EPRI Data, reference 7.

TABLE 21

TRENCH A COAL
MATERIAL COSTS AND PRODUCT REVENUE FOR INDICATED PRODUCT SLATE

Material	Cost	Product
Feed Coal	$22/tonne(1) clean coal	Light Syncrude
Plant Fuel (washery rejects(2))	- 0 -	1.87 bbl x $36 = $67.30
Reformer Feed (C_1-C_4 gas product)(3)	- 0 -	
Total Material Cost	$22/tonne or $11.76/bbl	Total Revenue = $67.30/tonne $\frac{\text{Revenue}}{\text{Material Cost}}$ 3.06

(1) as tested for Fe exchange catalyst, 7.9% moisture, 28.8% ash, 75% combustible recovery, 1.8 tonnes ROM coal, 56% moisture + ash @ $10/tonne, beneficiation and drying @ $4/net tonne clean coal

(2) reject analysis as per Fe exchange test, 61.8% ash, dry basis

(3) 26.3% of clean coal calorific value, see Table 12.

FIGURE 1

SCHEMATIC DIAGRAM OF TUBING BOMB REACTOR

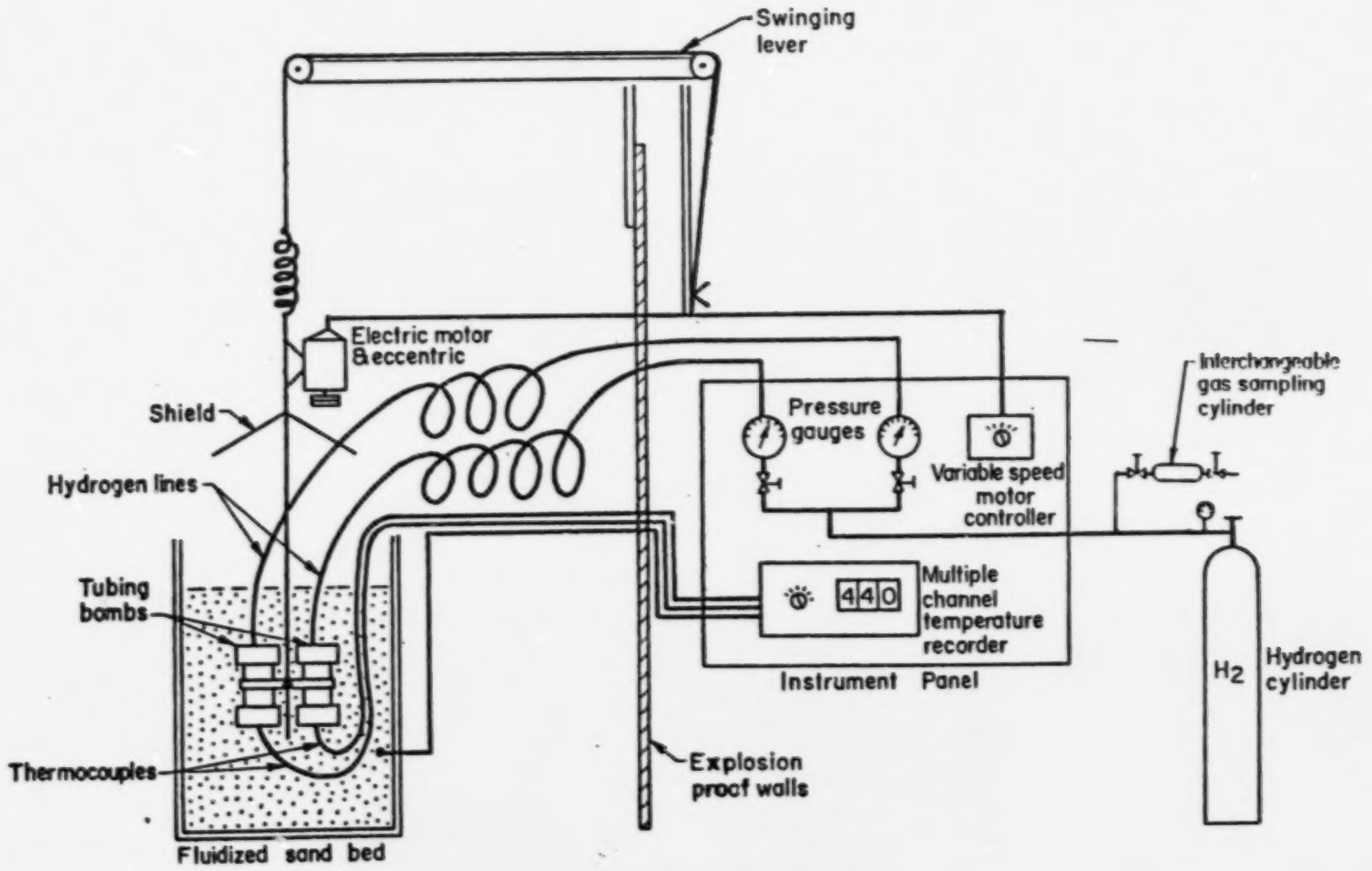


FIGURE 1

FIGURE 2

BC RESEARCH CONTINUOUS COAL LIQUEFACTION UNIT

Detailed Flow Diagram

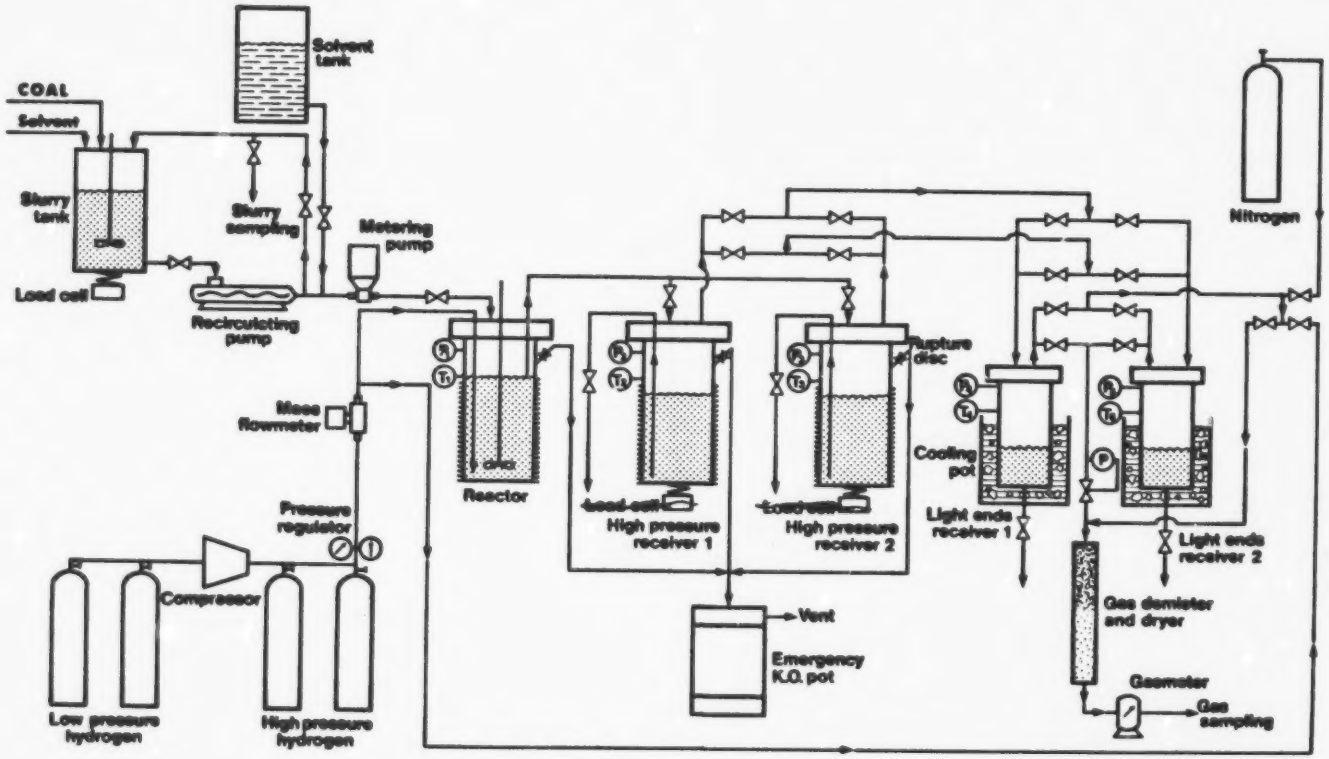


FIGURE 2

FIGURE 3

B.C. RESEARCH HYDROTREATER

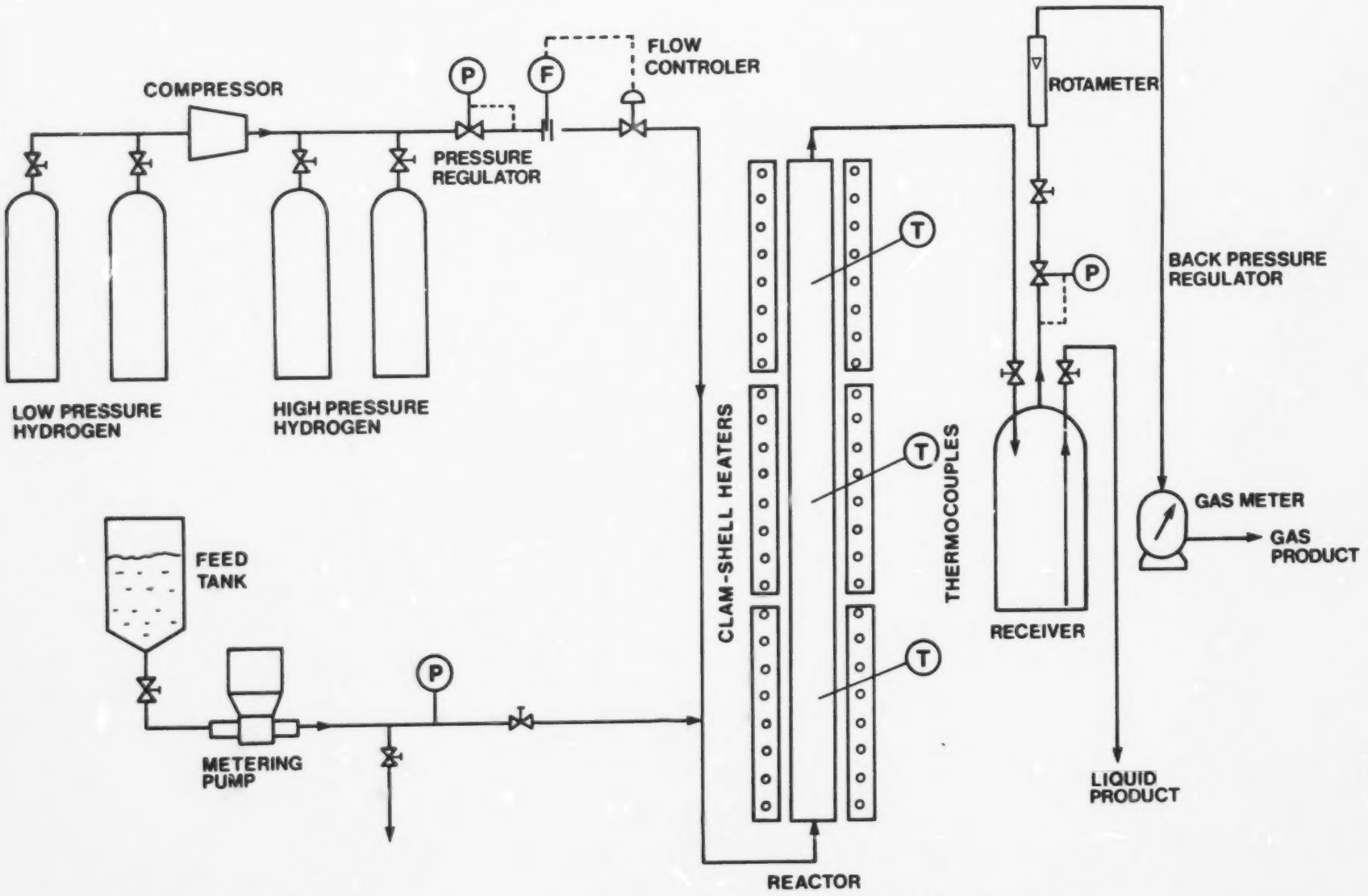


FIGURE 3

FIGURE 4
HYDROTREATER TEMPERATURE PROFILE - RUN 1

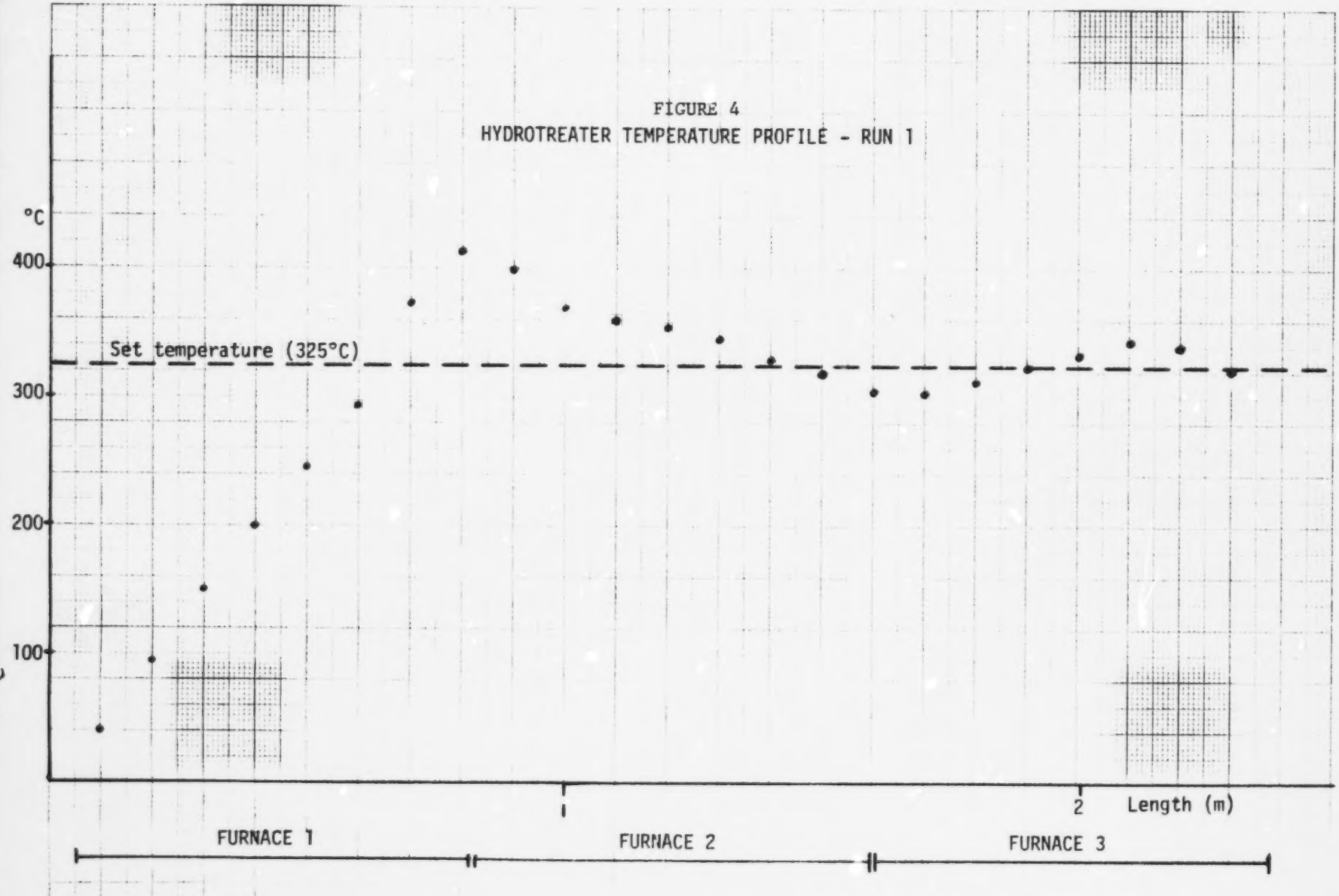


FIGURE 4

FIGURE 5

HYDROTREATER TEMPERATURE PROFILE - RUN 2

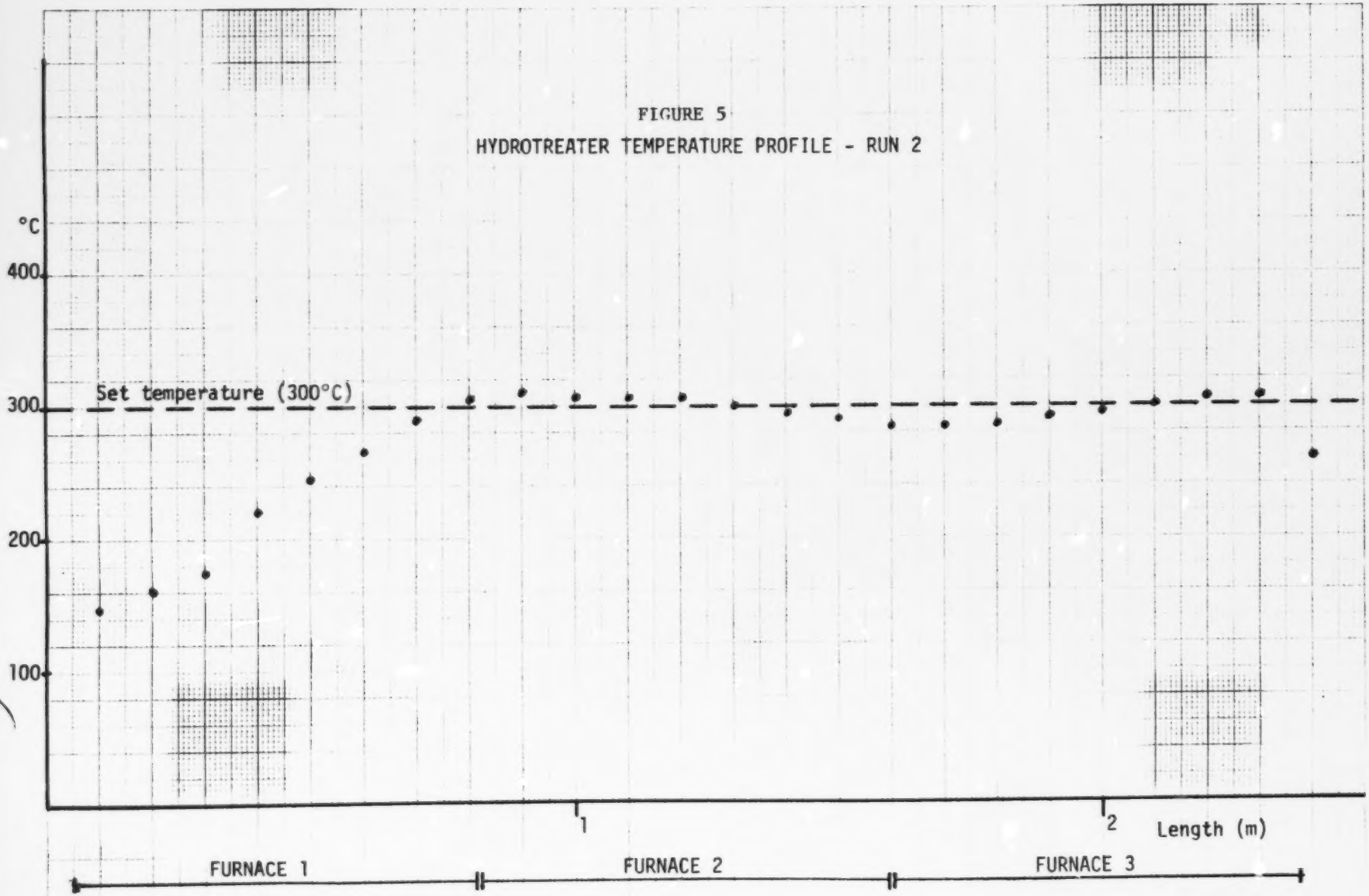


FIGURE 5

FIGURE 6
HYDROTREATER TEMPERATURE PROFILE - RUN 11

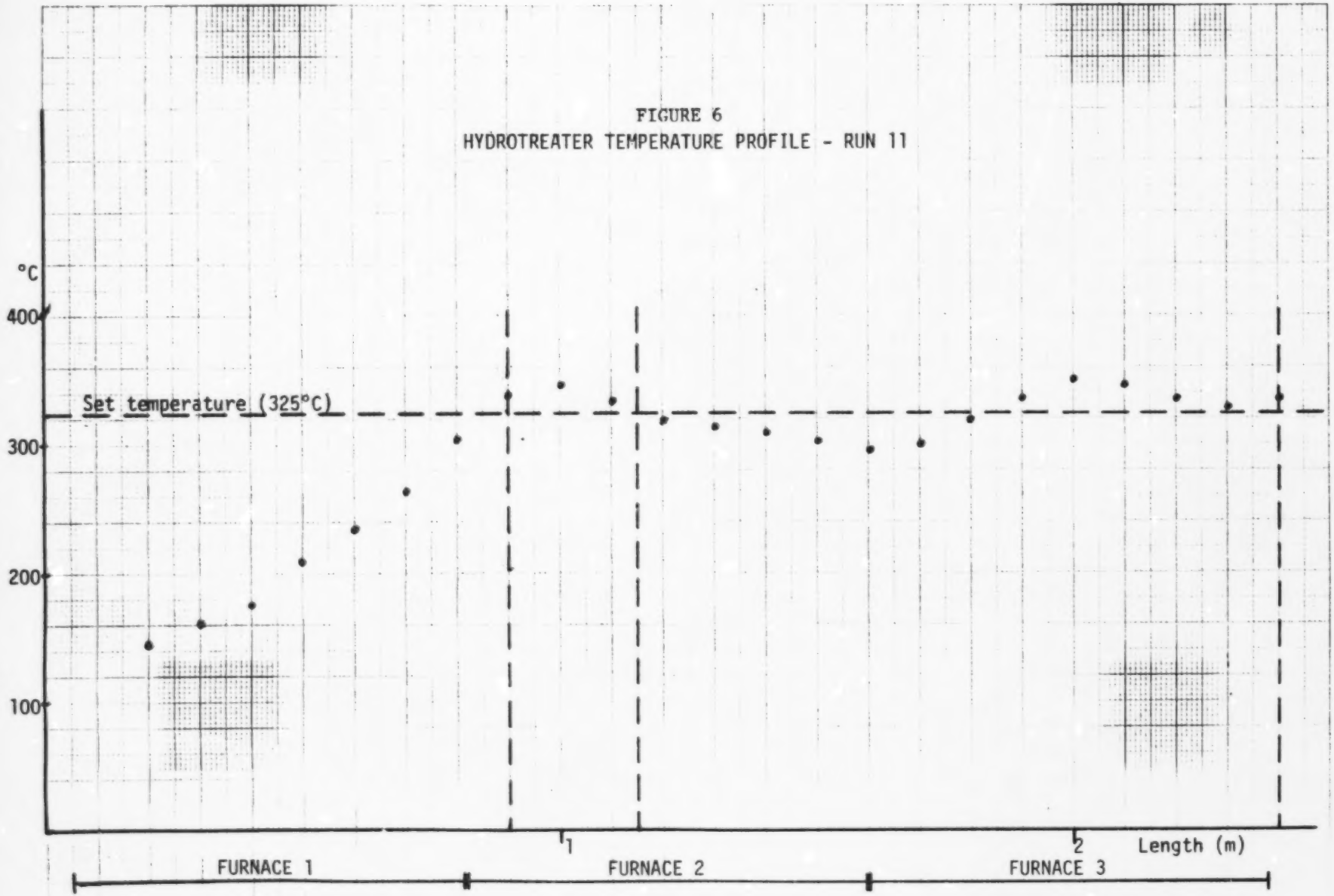


FIGURE 6

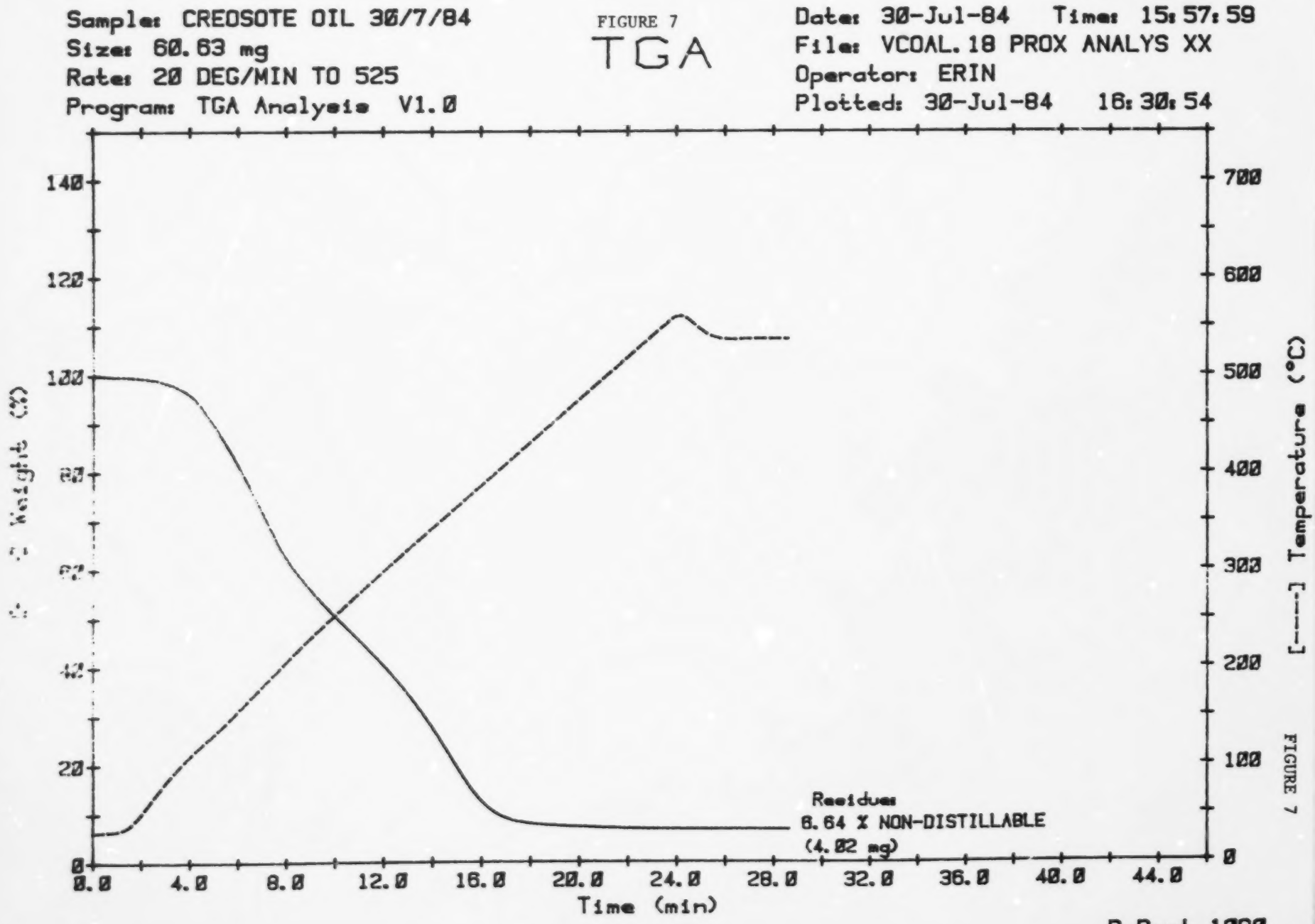

Sample: CREOSOTE OIL 30/7/84
Size: 60.63 mg
Rate: 20 DEG/MIN TO 525
Program: TGA Analysis V1.0
FIGURE 7
TGA
Date: 30-Jul-84 Time: 15:57:59
File: VCOAL.18 PROX ANALYS XX
Operator: ERIN
Plotted: 30-Jul-84 16:30:54
140
120
100
80
60
40
20
0
% Weight (%)
700
600
500
400
300
200
100
0
[---] Temperature (°C)
Residue
6.64 % NON-DISTILLABLE
(4.02 mg)
0.0
4.0
8.0
12.0
16.0
20.0
24.0
28.0
32.0
36.0
40.0
44.0
Time (min)
DuPont 1090

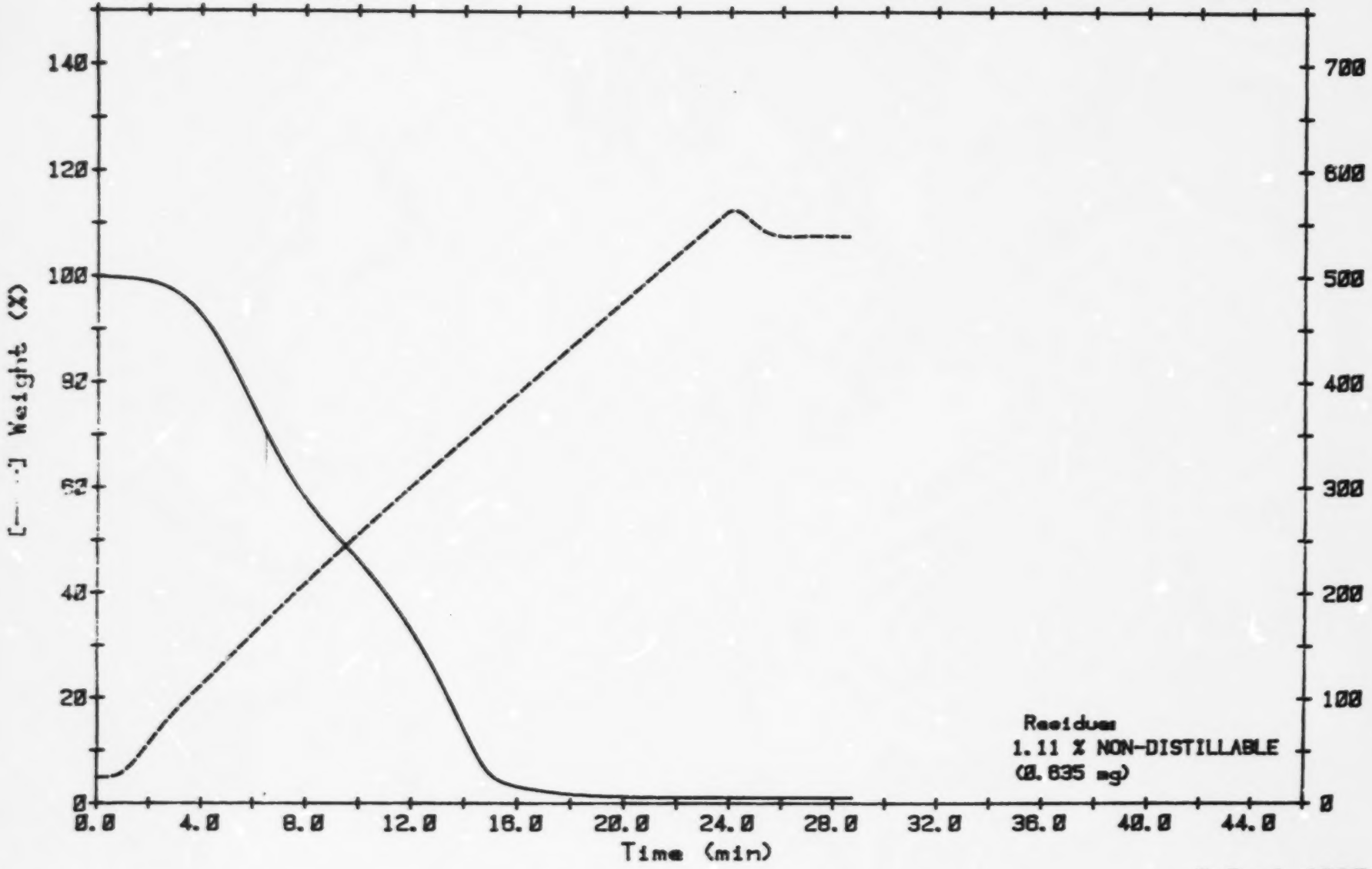
FIGURE 7

Sample: H16 HYDROTR. CREOSOTE
Size: 57.48 mg
Rate: 20 DEG/MIN TO 525
Program: TGA Analysis V1.0

FIGURE 8

TGA

Date: 31-Jul-84 Time: 8:05:17
File: VCOAL.19 PROX ANALYS XX
Operator: ERIN
Plotted: 31-Jul-84 9:01:48



DuPont 1090

FIGURE 8

APPENDIX 1

Operational Procedures for Continuous Liquefaction Unit

The liquefaction unit is operated on a single shift basis; startup, operation and shutdown were completed within (maximum) 11 h periods.

Feed preparation (see text) is conducted in advance.

From a cold, depressurized start, operational stages were as follows:

1. Reactor loaded with clean vehicle (or raw creosote).
2. Pressurized and heated to 440°C.
3. While reactor heating, flow on recirculation pump established to keep slurry in motion. (Full slurry tank weighed.)
4. Shortly before reactor on temperature, metering pump primed, with high pressure delivery valve to the reactor closed.
5. When reactor on temperature, delivery valve opened and pumping commenced.
6. Back pressure and gas flow controlled manually by metering valve.
7. Flow switched to second receiver train when fed ~ 1-1.5 kg of slurry.
8. Full receiver train depressurized (through the gas meter) and products discharged.
9. At the end of the run, heating and pumping stopped, and feed and exit valves closed. Reactor cooled with compressed air.
10. When cool, reactor and receivers opened to collect any residual product.

APPENDIX 2

Bulk Continuous Liquefaction Product Workup Procedure

1. Products were collected as they came out of the receivers in batches of ~ 1 kg, weighed and transferred into 500 ml plastic centrifuge bottles with tight-fitting closure.
2. Centrifugation was done at 2500 rpm for 20 minutes.
3. Centrifuge overflow was weighed and collected in a container.
4. If the amount of solid residue in the plastic bottles was small, the bottle was filled with products once more and centrifugation repeated in order to cut the final number of bottles.
5. Centrifuge underflow was mixed with THF (cake was thoroughly slurried in THF) in the bottle and centrifugation was repeated).
6. THF washings were collected in a pre-weighed 1 litre distillation flask.
7. THF washing procedure was repeated until the overflow was reasonally clean (usually 3 - 4 washings).
8. THF washings were distilled on a short distillation column, under N_2 blanket to minimize oxidation, to 100°C.
9. Contents of distillation flask were cooled down (under N_2) and weighed, precipitated solids were slurried with the liquid and the slurry was transferred into centrifuge bottles.
10. Centrifugation was carried on as above. Liquid was collected and weighed (THF recovered liquid).
11. Sludge weight is difference between liquid weight before and after centrifugation.
12. Sludge was reserved for addition to next run.
13. THF washed solids from point 7 were dried at 40°C and weighed.

APPENDIX 3

Operational Procedures for Continuous Hydrotreater

The continuous, fixed bed hydrotreater was operated on a single shift basis; startup, operation and shutdown were within (maximum) 11 hour periods. From a cold, de-pressurized start, operational steps were as follows:

- Tare feed tank and load initial charge of liquid feed,
- flush, pressurize and leak test hydrotreater column,
- initiate heating with manual control of the 3 zone heaters,
- manually adjust effluent gas flowrate to minimum gas flow through the system,
- prime feed pump
- when reactor reaches the target temperature as indicated by the 3 fixed therocouples, switch to automatic temperature control
- start liquid feed and feed preheater
- adjust back pressure and exhaust gas flow (manual)
- at apparent steady state, use moveable axial thermocouple to determine reactor temperature profile,
- at end of run, stop liquid feed, manually reduce exhaust gas to minimum flowrate, turn off heaters, and cool to ~200°C before shutting off gas flow,
- weigh residual feed in tank,
- manually drain receiver tank (slowly, to control foaming), and weigh product. (Total feed weight can be obtained from load cell trace). The column was not normally drained between runs.

APPENDIX 4

Manufacturer's Recommended Catalyst

Presulphiding Procedure

AERO® HDS Hydrotreating Catalysts Presulfiding Procedure

Worldwide Catalyst Department
Industrial Chemicals Division
Wayne, New Jersey 07470

®Trademark of American Cyanamid Company

preferred commercial presulfiding procedure

(liquid feed)

1. After the catalyst is loaded, purge the system thoroughly with inert gas after pressure testing. Adjust the reactor pressure to 200-500 psig (1.38-3.45 MPa gauge) with dry hydrogen. Establish maximum once-through hydrogen rate and heat to 300°-350°F (150°-175°C) at 100°-120°F/hr (55°-65°C/hr). Maintain maximum cooling on condensers to remove as much water as possible in the separator. Drain water from the separator as needed. Maintain hydrogen purge at 300°-350°F (150°-175°C) for at least 1 hour and until no more free water is taken out at the separator.

2. Establish normal recycle or once-through treat gas rate. Introduce virgin feedstock (such as kerosine or distillate) spiked with 1-2 wt % sulfur. Feedstock containing unsaturated compounds should not be used. Final boiling point should be 640°F (340°C) or less. Common sulfiding agents are carbon disulfide (CS_2), dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and light mercaptans (R-SH). In determining the total requirement of sulfiding agent, the sulfur content of the high boiling feedstocks should not be included since at the initial low temperatures and low catalyst activity it is nearly impossible to predict accurately the quantity of feedstock sulfur that will enter into presulfiding reactions. (For guide to quantity of sulfiding agent required, see Figure 1 or Table 1 and Figure 2 or Table 2.) Sulfiding is generally done at a LHSV of 1-2 hr^{-1} unless on units such as naphtha prereformers, this exceeds a 50% turndown. In high LHSV units with once-through treat gas, sulfiding at half the normal feed rate is suggested. Initial sulfiding of the catalyst should normally be done at 300°-400°F (150°-205°C) by adjustment of the reactor inlet temperature. Some sulfiding compounds, e.g. dimethyl sulfide may require up to 450°F (230°C) reactor temperatures to initiate sulfiding. Care should be taken not to exceed 500°F (260°C) anywhere in the catalyst bed during initial sulfiding. Depending upon feed sulfur concentration and the resultant exotherm, reactor temperatures could reach into an undesirable 600°-700°F (315°-370°C) range. In this high range, coking and promoter metal oxide reduction may occur before sulfiding is complete. Sulfur concentration should be controlled as required to hold bed temperatures below 500°F (260°C). Additions of sulfiding agents to the charge oil should be on the low side (1.0 wt % S) initially since excessive sulfur injection might hamper temperature control. During presulfiding operation, hydrogen sulfide removal by amine treatment or any other method should cease until the catalyst has been fully presulfided.

preferred commercial presulfiding procedure

(liquid feed)

3. Continue to sulfide the catalyst until a copious breakthrough of H_2S is observed. In the early stages of sulfiding, the H_2S in the recycle gas will remain low, typically 5-10 grains of H_2S per 100 SCF (80-160 ppm vol H_2S). When breakthrough occurs, H_2S concentration will rise rapidly. Most refiners wait until the concentration reaches 200 grains of H_2S per 100 SCF (3200 ppm vol H_2S) in the recycle gas before acknowledging breakthrough. The concentration of H_2S in the recycle can be measured by a device such as a Drager tube. The H_2S content in the recycle gas should be checked at least once every hour prior to breakthrough.

4. After breakthrough of H_2S, stop sulfur injection and continue to circulate recycle gas (on units with recycle) in closed system while monitoring the H_2S level. If after one (1) hour, the H_2S concentration remains high, initial sulfiding can be assumed completed. If H_2S level drops significantly after an hour, sulfur is still being taken up and further sulfiding is required. Also ascertain quantity of sulfiding agent consumed. About half of required sulfiding compound should be consumed before initial H_2S breakthrough happens. This is an important consideration for once-through treat gas units where premature H_2S breakthrough might not be otherwise recognized.

5. A second stage of sulfiding is desirable to assure complete sulfiding. This may be done by raising the temperature to 550°-600°F (288°-315°C) at 25°F/hr (15°C/hr) and reinjecting sulfur at the previous levels. Do not exceed the anticipated start of run temperature during the second sulfiding stage.

6. When the second breakthrough occurs, injection should be continued for 30 minutes or until 0.11 pounds of sulfur per pound of catalyst has been injected to ensure completeness of sulfiding. Figure 3, which does not account for time to raise temperatures or stabilize conditions, serves as a guide of minimum time required to complete presulfiding.

7. When presulfiding is complete, remove H_2S from recycle gas by placing recycle gas scrubber in service (if available), or reduce H_2S level below 1 vol % by purging with hydrogen.

8. Adjust reactor temperature, pressure and feed rate to normal or anticipated start of run conditions.

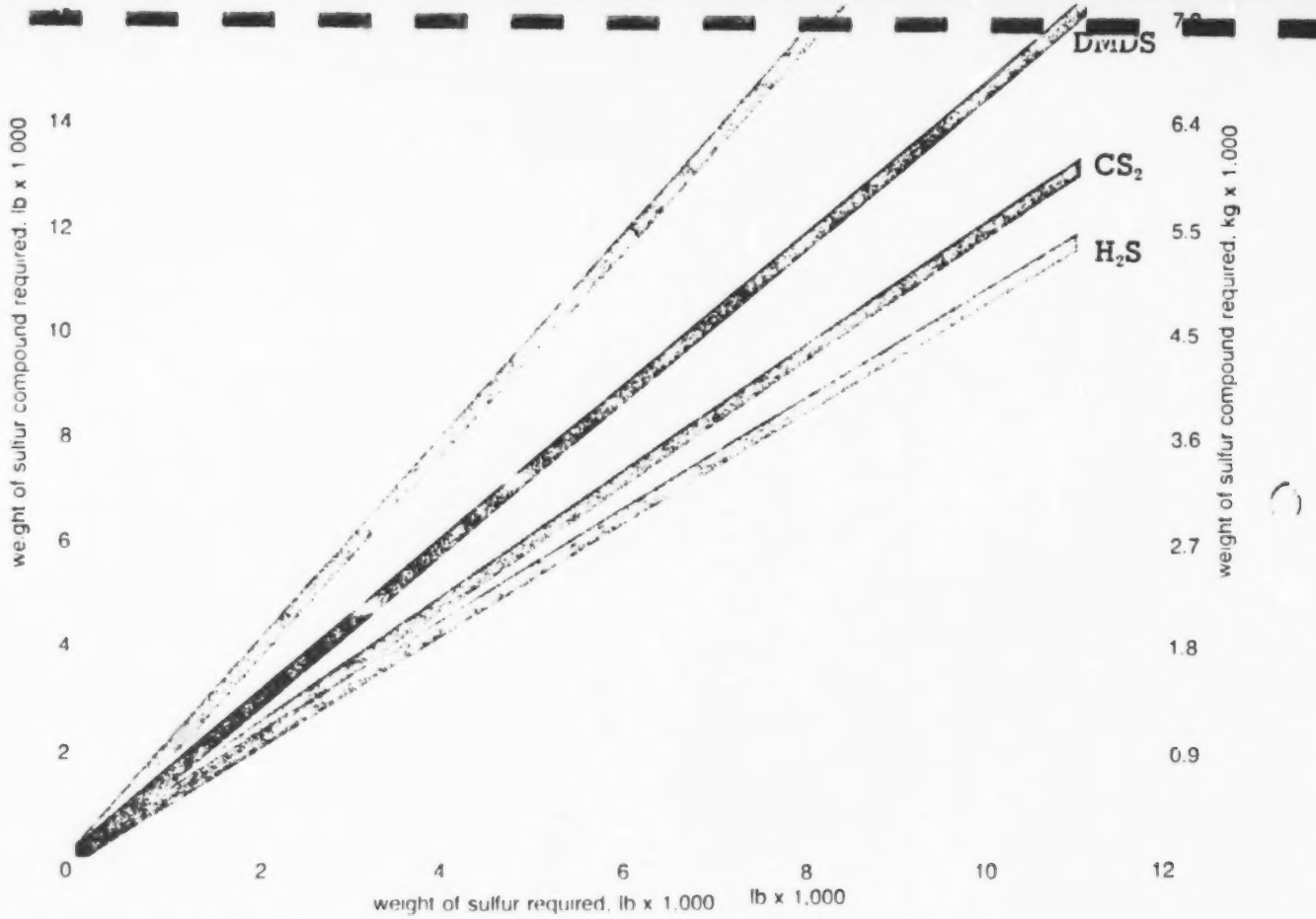


Table 2: Presulfiding – Quantity of sulfiding compound required

sulfur required		DMS (51.6%S)		DMDS (68.1%S)		CS_2 (84.2%S)		H_2S (94%S)	
lb	kg	lb	kg	lb	kg	lb	kg	lb	kg
110	50	213	97	162	73	131	59	117	53
440	200	853	388	646	294	523	238	468	213
880	400	1,705	775	1,292	587	1,045	475	936	425
1,320	600	2,558	1,163	1,938	881	1,568	713	1,404	638
1,650	750	3,198	1,453	2,423	1,101	1,960	891	1,755	798
2,200	1,000	4,264	1,938	3,231	1,468	2,613	1,188	2,340	1,064
2,750	1,250	5,329	2,422	4,038	1,836	3,266	1,485	2,926	1,330
3,300	1,500	6,395	2,907	4,846	2,203	3,919	1,781	3,511	1,596
4,400	2,000	8,527	3,876	6,461	2,937	5,226	2,375	4,681	2,128
5,500	2,500	10,659	4,845	8,076	3,671	6,532	2,969	5,851	2,660
8,250	3,750	15,988	7,267	12,115	5,507	9,798	4,454	8,777	3,990
11,000	5,000	21,318	9,690	16,153	7,342	13,064	5,938	11,702	5,319

APPENDIX 5

Tubing Bomb Conversion Calculations

1. Gravimetric

$$\% \text{ conversion} = \left(1 - \frac{\text{DAF residue}}{\text{DAF coal}}\right) \times 100$$

2. Ash Balance

$$\% \text{ conversion} = \frac{A - a}{A(100-a)} \times 10^4$$

A = Dry ash in residue (not %)
a = Dry ash in coal.

3. Calorific Value

$$\% \text{ C.V. Conversion} = \left(1 - \frac{R \times CVR}{C \times CVC}\right) \times 100$$

R = amount of residue (g)
C = amount of coal (g)
CVR = calorific value of residue (cal/g)
CVC = calorific value of coal (cal/g)

EXAMPLE OF CALORIFIC VALUE CONVERSION CALCULATION FOR TUBING BOMB RUNS

Run B 517/3

	C.V. (cal/g)	Amount
Coal	4273	10.0 g
Residue	1568	3.4 g

$$\% \text{ Conversion} = \left(1 - \frac{3.34 \times 1568}{10 \times 4273} \right) \times 100 = 87.7$$